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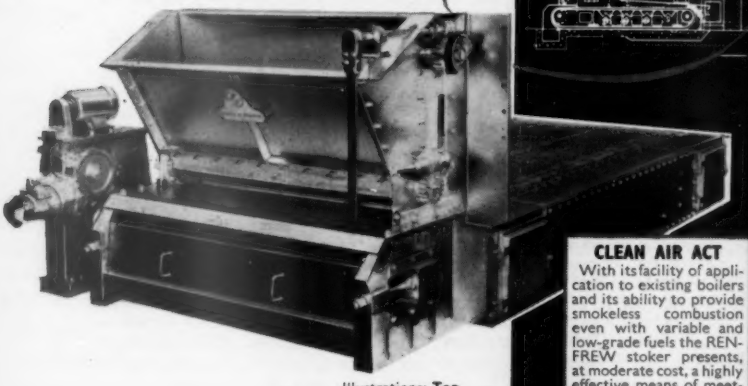

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BUTTERWORTHS SCIENTIFIC PUBLICATIONS

Emeritus Professor Sir Alfred C. Egerton, F.R.S.

It is with great regret that we record, as we go to press, the sudden death abroad of Sir ALFRED C. G. EGERTON, F.R.S., latterly General Editor of *FUEL* and *COMBUSTION AND FLAME*. An appreciation of his life and work will appear later.

*Diffusion of Gases through Coal**

P. G. SEVENSTER

The total diffusion coefficient for a number of gases is of the order of 10^{-13} cm²/sec for powdered coal and 10^{-11} for flow in a solid plug. From these results it may be concluded that the coal substance is almost impermeable to gases and that the higher permeation rates observed with solid plugs are due to microcracks and fissures in the coal. A comparatively large surface flow is observed with strongly adsorbed gases. The flow of less strongly adsorbed gases is probably governed by molecular streaming; it also increases with porosity.

IT IS generally realized that the rate of heterogeneous reactions, especially where a porous solid is involved, is very largely if not wholly determined by the rate of diffusion of gaseous reactants to, or of gaseous products from, the solid surface.

This applies also to the oxidation of coal irrespective of whether the reaction takes place at ambient temperature (spontaneous heating) or at elevated temperatures (combustion).

It is somewhat surprising therefore that, although much fundamental work has been done on spontaneous heating and combustion, and work on the porous structure of coal was done in this connection, very little work seems to have been done to establish diffusion coefficients of gases in coal directly.

Reference can only be made to the work of IVON GRAHAM[1] who studied the diffusion of gases in solid slabs of coal. Unfortunately he used gases saturated with water vapour and this makes it very difficult to analyse and interpret his results. His measurements suggest, however, that coal is almost impervious to gases.

A. G. MERTIN[2] calculated average pore diameters from measurements of the flow rate of hydrogen through solid coal discs. He also found that gases permeate extremely slowly through the mass of the coal substances. Reference may also be made to the studies of P. ZWIETERING and others[3] and of A. S. JOY[4] who calculated a diffusion coefficient for methane from rate of adsorption data.

Because of this paucity of publications on the subject, it was found necessary to conduct the investigation described in this paper when information on diffusion coefficients of some strongly adsorbed gases was required in the course of other studies on coal at this Institute. Two methods of approach appeared feasible:

(*a*) The calculation of diffusion coefficients from the results obtained in adsorption kinetics studies that had already been done at this Institute, and
(*b*) Direct quantitative measurements of the flow of gases through coal.

* *Report No. 9* of 1958 (R).

The former approach would yield results more rapidly but the latter would have the advantage that the diffusion of gases that are only slightly adsorbed could also be studied. Furthermore, it could be used to obtain some check on the reliability of the former method.

COALS USED IN THE INVESTIGATION

The coals used in this investigation may be characterized by typical proximate analyses and data on physical structure applying to the samples actually used as shown in *Table 1*. Adsorption rate data for coals A, B and C were available from earlier studies[5] and coals B, C and D were used for flow measurements. The porosities and surface areas of these coals had also been determined[6].

Table 1. Analytical data on coals used in the investigation

Coal sample	*% ash*	*Air-dried moisture*	He *density*	*Porosity* cm³/g*	*Internal surface area† m²/g*
A	24·2	7·5	1·36	0·176	181
D	18·3	5·6	1·36	0·146	161
B	21·8	2·8	1·35	0·121	110
C	13·1	1·8	1·33	0·085	85

* Calculated from helium and mercury densities.
† Calculated from heat of wetting measurements. F. A. P. MAGGS and others have established that the heat of wetting per unit area of a coal surface is about 0·1 cal/m².

(A) CALCULATION OF DIFFUSION COEFFICIENTS FROM THE RESULTS OF ADSORPTION KINETICS STUDIES

The experimental results available for these calculations were confined to those obtained in the study of the adsorption of oxygen and water vapour[8] on coals of varying rank.

Considering the various possibilities of approach, that of A. F. WARD[9] appeared to merit close consideration. Ward had analysed the results of rate of adsorption experiments (hydrogen on copper oxide) by means of Fick's diffusion law and found that the quantity of gas adsorbed was proportional to the square root of the time. R. M. BARRER[10] applied Ward's findings to the adsorption kinetics in zeolite crystals, and derived the following equation

$$(Q_t - Q_0)/(Q_\infty - Q_0) = (2S/V)(Dt/\pi)^{\frac{1}{2}} \quad \ldots\ [1]$$

where D is the diffusion coefficient Q_0, Q_t and Q_∞ are the quantities of the gas adsorbed in a constant pressure system at the times 0, t and at equilibrium, respectively. S is the external surface area of the sample and V is its volume.

Samples of coal evacuated at 120°C for about 16 hours were always used. It was assumed that the samples had been completely degassed so that $Q_0 = 0$. By plotting Q_t/Q_∞ against $t^{\frac{1}{2}}$ the diffusion coefficient can be calculated from the slope of the straight line so obtained.

The volume of a sample is found from the helium density, and the surface area can be calculated by a method developed by Barrer[10], the required information being obtained from the $t^{\frac{1}{2}}$ versus Q_t/Q_∞ plots of the low

temperature (−185°) oxygen adsorption rate data. Values of about 1×10^4 cm²/g were obtained.

J. W. McBain[11], G. Damköhler[12], R. M. Barrer and E. K. Rideal[13] and E. Wicke[14] have also proposed equations relating the diffusion process to the adsorption rate. These equations are formally not very different from the equation derived by Ward and quoted as equation 1 in the modified form suggested by Barrer.

Determination of adsorption rates

Oxygen adsorption rates were determined in a conventional constant volume adsorption system. The adsorption of oxygen by coal is an extremely slow process after an initial reasonably rapid stage has been passed. At 30° and 67 cm of mercury pressure equilibrium was only approached after about 100 h. Experiments had been carried out at various constant pressures at 30° and 60°C on about 5 g of sample (−60 mesh B.S.S. size).

When plotting Q_t/Q_∞ against $t^{\frac{1}{2}}$, curves of the form shown in *Figure 1* were obtained.

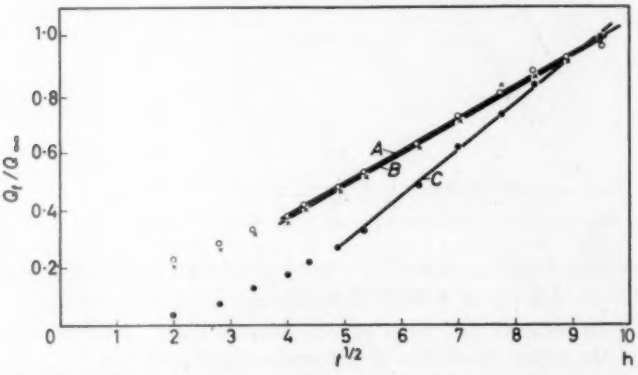

Figure 1. Rate of adsorption of oxygen by coal at 30°C and 67 cm of mercury pressure

During the initial stages of the adsorption, the $t^{\frac{1}{2}}$ law is not valid but after about 9 h a straight line relationship exists and continues throughout until equilibrium is approached. Results computed from data obtained from the straight line region of the curve by means of equation 1 are given in *Table 2*.

The water vapour adsorption rate measurements were made by means of quartz microbalances. Before conducting experiments the coal samples (about 1 g of coal −60 mesh B.S.S. size) were outgassed in the apparatus by heating to 100°C in a vacuum to constant weight.

The adsorption of water vapour is more rapid than that of oxygen, about 70 per cent of the equilibrium amount is adsorbed during the first 100 min. Thereafter the adsorption is slow, equilibrium being reached after about 24 h.

The results of experiments conducted at 25°C and 21 mm of mercury pressure were used to plot $t^{\frac{1}{2}}$ against Q_t/Q_∞ as shown in *Figure 2*. These curves are typical of those obtained for the experiments conducted at various temperatures and pressures with water vapour. It will be noted that a straight line relationship exists in the earlier stages of the adsorption but that, as might be expected from theoretical considerations, a deviation occurs as equilibrium

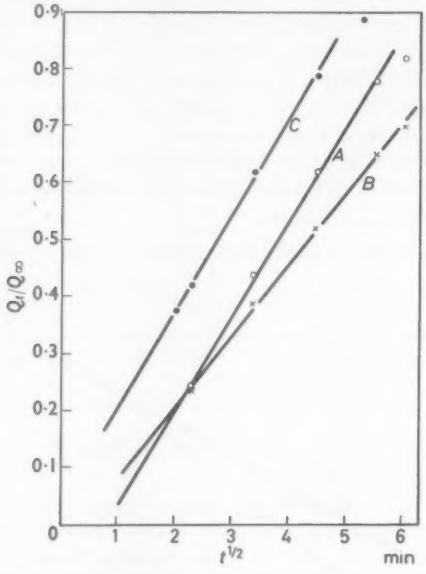

Figure 2. Rate adsorption of water vapour by coal at 25°C and 2·1 cm of mercury pressure

is approached. Results computed by means of equation 1 from experiments performed at 25°C are also given in *Table 2*.

The results indicate that water vapour diffuses about 10 times faster than oxygen at the stated conditions of temperature and pressure.

Since water and oxygen are both fairly strongly adsorbed this difference is probably due to such factors as affinity, degree of coverage and the relative pressure. The effects of temperature and pressure discussed below also demonstrate a difference in the flow behaviour of oxygen and water vapour.

Table 2. Diffusion coefficients of water vapour (21 mm of mercury and 25°C) and oxygen (30°C and 67 cm) for three different coals

Coal sample	*Porosity* cm^3/g	*Diffusion coefficient,* cm^2/sec	
		Oxygen	*Water*
A	0·176	$4{\cdot}5 \times 10^{-14}$	$5{\cdot}2 \times 10^{-13}$
B	0·121	$4{\cdot}5 \times 10^{-14}$	$4{\cdot}8 \times 10^{-13}$
C	0·085	$6{\cdot}5 \times 10^{-14}$	$6{\cdot}4 \times 10^{-13}$

Effect of pressure

With oxygen, the diffusion coefficient seems to be independent of the pressure. Plots of Q_t/Q_∞ against $t^{\frac{1}{2}}$ for measurements at 10, 40 and 67 cm of mercury coincide closely.

There is evidence that the predominant pore size of coal is of molecular dimensions which suggests that the flow of oxygen in the gas phase is by molecular streaming which is independent of pressure. But because oxygen is strongly adsorbed, one would expect surface flow also to occur. It appears, however, that although the rate of adsorption increases with pressure, no corresponding increase in the surface flow takes place. This effect is probably due to the fact that as the pressure increases the surface will become densely occupied thereby preventing the molecules from moving freely across the surface.

Water vapour shows a decided enhanced flow with increased pressure. Results obtained for three different coals are given in *Table 3.*

Table 3. Effect of pressure on the diffusion coefficient of water vapour at 25°C

Coal sample	*Diffusion coefficient* $\times$ 10^{13} *cm²/sec*			
	Pressure, mm of mercury			
	4·7	10·2	12·2	21·0
B	2·2	2·2	3·3	4·8
C	2·6	3·5	4·5	6·4
A	1·3	2·6	2·4	5·2

Assuming again that the flow is by molecular streaming and surface flow, it seems that here the surface flow is dependent on pressure. The relatively weak attractive forces between water and coal and the high dipole attraction between the water molecules may account for the pressure dependence of the water vapour flow.

Effect of temperature

In the experiments conducted at a pressure of 21 mm of mercury and 25°, 38° and 60°C, it was found that the rate of adsorption of water vapour, as well as

Table 4. Diffusion coefficient of water vapour at 21 mm of mercury and different temperatures for three coal samples

Coal sample	*Diffusion coefficient* $\times$ 10^{13} *cm²/sec*			*Average activation energy kcal/mol.*
	Temperature, °C			
	25	38	60	
B	4·8	5·8	6·4	2·8
C	6·4	7·6	8·2	2·4
A	5·2	6·4	7·4	2·1

the equilibrium amount of water adsorbed, decreased with increase in temperature. However, due to the relative rate of decrease of these quantities, the calculated diffusion coefficient was actually found to increase with temperature as shown in *Table 4*.

By plotting log D against $1/T$ straight lines are obtained the slopes of which correspond to the activation energies given in *Table 4*.

Since molecular streaming is only dependent on $t^{\frac{1}{2}}$, and the results clearly indicate an exponential dependence on the temperature, it must be concluded that a considerable proportion of the total diffusion must be by surface flow which is an activated process.

The quantity of oxygen adsorbed at any time, as well as the amount adsorbed at equilibrium, were found to change with temperature in such a way that the Q_t/Q_∞ versus $t^{\frac{1}{2}}$ curves at 30° and 60°C for each of the coals studied, coincided closely. However, since there are indications that a definite chemical reaction takes place between oxygen and coal at about 60°C, no further analysis of the results can be made.

Effect of porosity

The coals used for the adsorption rate measurements (A, B and C) provided a fair range of porosities. According to the results in *Table 2*, the diffusion coefficients of oxygen and water vapour did not change appreciably at the experimental conditions under which the measurements were made.

(B) CALCULATION OF DIFFUSION COEFFICIENTS FROM RESULTS OF GAS FLOW RATE STUDIES

Equation 1 yields an overall or total diffusion coefficient, i.e. it includes coefficients for Poiseuille flow, Knudsen flow and surface diffusion.

The relative contributions of these processes to the total flow of a gas depend on various factors such as the pore size, the size and weight of the diffusing gas molecule and the adsorption coefficient.

Poiseuille flow and Knudsen diffusion (molecular streaming) depend primarily on the pore diameter. The former occurs in passages with diameters that are large compared with the molecular mean free path, and the latter predominates in pores having diameters that are comparable with the mean free path.

Now, earlier work[6] had proved that a high percentage of the pore volume of the coals studied was due to to pores having diameters of the order of 20 Å and that much finer pores largely contribute to the total surface available for adsorption.

The extremely slow adsorption of gases frequently observed with coal may be due to surface effects in these small pores and to changes in pore diameter due to adsorption.

Under such circumstances surface diffusion that depends on the mobility of the adsorbed molecules may contribute to an appreciable extent to the total rate of diffusion.

In recent years attention has been drawn to the quantitative effects which the mobility of molecules in adsorbed layers have on the total flow of gases and vapours through porous media. In this connection special attention may be drawn to the work of R. M. TOMLINSON and E. A. FLOOD[15], P. C. CARMAN *et al.*[16, 17] and R. M. BARRER *et al.*[18, 19].

Although the available adsorption rate data for oxygen and water could have been analysed by methods proposed by Damköhler[12] and Wicke[14] to obtain information on surface diffusion, it seemed preferable to study diffusion phenomena and especially the influence of surface effects on them by methods based on the direct measurements of flow through the solid material. This would have the advantage of extending the study to less strongly adsorbed gases. Furthermore, actual flow rate measurements through coal would be of practical interest.

The methods of Barrer[18, 19] and of Carman[16, 17] were considered. They require more or less the same experimental procedure but Barrer's method involves the measurement of the time taken before a steady of flow occurs ('time lag'), as well as measurement of the rate of transport during the steady state. Since it was difficult to follow the course of the transient flow due to the very small flow rate, the measurements of the time lag were liable to error. Therefore this method was considered to be less suitable for the study of the flow of gases through solid coal than Carman's method which involves only the measurement of the flow during the steady state while the pressures on each side of the plug are kept constant. This method also requires a knowledge of the porosity of the substance of the plug and of the amount of gas adsorbed by the coals at the temperatures and pressures at which the flow measurements were made.

Since the pores encountered in coal are extremely small, the equation proposed by Carman for determining the flow in micropores may be simplified somewhat by neglecting the viscous term for flow in the gas phase. The equation may be written:

$$P_s = D_s \rho(1 - \epsilon)(v/\Delta p)$$
$$= (WL/\Delta pA) - (W_1 L/\Delta p_1 A)(M_1 T_1/MT)^{\frac{1}{2}} \quad \ldots . [2]$$

where P_s is the surface permeability and D_s is the surface diffusion coefficient, ρ is the density of the sample and ε is the porosity. The pressure gradient across the plug is represented by Δp and v is the difference between the quantities adsorbed on each side of the plug at the prevailing pressures. The quantities adsorbed are obtained from isotherms.

The surface permeability is the difference between the total permeability, $(WL/\Delta pA)$, and the 'calculated gas permeability', $(W_1 L/\Delta p_1 A)(M_1 T_1/MT)^{\frac{1}{2}}$. W_1 is the flow rate* in ergs/sec of a non-adsorbed gas with molecular weight M_1. A is the cross sectional area of the plug and L is its length (or thickness).

EXPERIMENTAL PROCEDURE

The experimental determination of diffusion constants of gases through coal is complicated by a number of factors.

* To convert flow rate to millimoles/sec as used by Carman *et al.*[16, 17] multiply ergs/sec by $1000/RT = 1{\cdot}20 \times 10^{-5}/T$, see page 411.

As one object of the investigation was to obtain some information on the flow of gases in the solid coal, it was considered preferable to work on discs cut from solid blocks rather than on compacted plugs of granular coal samples, although the latter would enable one to have a more truly representative sample, say, of a coal seam.

On the same grounds one would have to ensure that the test piece was free from cracks or fissures, although it is recognized that these very probably play an important role in the flow of gases in the virgin seam or in lumps of coal, e.g. during oxidation (combustion).

The procedure finally adopted for preparing test pieces was to select typical lumps of coal (plus 4 in.) from the run-of-mine coal produced at selected collieries. The lumps were cut along the bedding plane by means of a high speed masonry saw to produce a plane surface. Cores of about 2·6 cm diameter were then produced from the prepared lumps by drilling holes vertically to the bedding plane with a small diamond core drill.

Discs, 2 to 3 mm thick, were cut from the cores with a hack saw and these were then ground to the final thickness* and diameter (2·6 cm) on a plate of glass using carborundum grinding powder.

Preliminary experiments proved that the rate of passage of gas through discs of 2 mm thickness was so low that it was impracticable to use them.

On the other hand discs of about 0·5 mm thickness had insufficient mechanical strength to withstand the pressure difference that had to be used to ensure flow, and invariably ruptured. This lack of mechanical strength also placed an upper limit on the diameter of the discs.

Practically all the work therefore was done on discs of about 1 mm thickness and a diameter of 26 mm.

All the coals tended to swell to some extent when adsorbing gas or vapour and to contract during outgassing. With coals having air-dried moisture contents of the order of 7 per cent and higher, the contraction was so marked that cracks invariably developed in the discs.

The flow rate measurements had, therefore, to be confined to coals having air-dried moisture contents below 6 per cent, i.e. on samples B, C and D of *Table 1*.

Mounting and testing of discs

A glass tube (*A* in *Figure 3*) was flared out at one end to a diameter of 16 mm and the surface was ground flat. The coal discs were cemented to this tube.

As the outgassing of the discs had to be done at a reasonably high temperature, a cement was required that would not become unduly soft at these temperatures while remaining sufficiently plastic at ambient temperature to allow for small expansion and contraction of the coal with adsorption and desorption of vapours or gases. After trying various cements 'Vitacote', having a softening point well above 120°C, was found suitable.

* Prepared in the Institute's coal petrology section.

Before sealing on any disc, it was examined under a low power microscope for soundness. After sealing on, the tube was connected to a vacuum system and the seal and the surface of the disc were tested for leaks by probing with a high frequency leak detector. The tests were made with a short spark length in a darkened room.

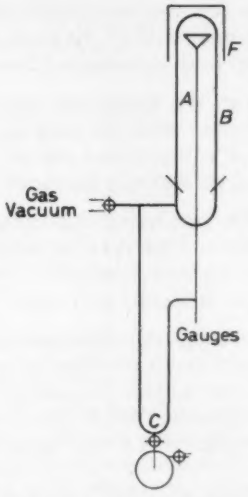

Figure 3. Apparatus used for measuring gas flow rates through coal discs

Apparatus—The apparatus used is shown diagrammatically in *Figure 3*. *A* represents the glass sample tube to which discs were cemented. This tube was sealed on to the apparatus. The cover tube *B* with ground-glass joint provided an easy means of getting at and changing sample tubes.

The mercury cut-off *C* was provided to allow simultaneous evacuation on both sides of the disc. This reduced the pumping time considerably. The cut-off was also used as a manometer.

The coal disc could be maintained at higher than room temperature by slipping a small electrically heated furnace *F* over the tube *B*.

As the gas flow rate was very low even with 1 mm coal discs, the apparatus was designed to measure flow rate in terms of the increase in pressure on the low pressure side of the disc*, while pressure on the other side was kept constant.

Due to the low rate of flow it was found unnecessary to provide an automatic pressure control device on the high pressure side. The pressure on the low pressure side remained so low that the pressure gradient (Δp) could be considered to be equal to the applied pressure.

To be able to measure such small increases in pressure, use had to be made of a McLeod gauge. In the water vapour experiments a Pirani gauge was also used to measure water vapour pressure.

To obtain the correct setting of the mercury on the calibration mark, a fine adjustment control provided on the mercury reservoir of the gauge was

* i.e. expressed as product of volume of vessel and pressure in dynes/cm².sec; absolute units—therefore equivalent to ergs/sec.

used in conjunction with a cathetometer. The cathetometer was also used to determine the difference in the height of the mercury columns of the McLeod gauge.

Outgassing of samples

A specific disc was usually retained in the apparatus until experiments had been done with all the gases selected for this study. Outgassing was practised on all fresh samples and between experiments with various gases.

With the apparatus assembled and cut-off *C* open, the apparatus was evacuated while the coal disc was maintained at 120°C. From time to time cut-off *C* was closed and the rate of pressure rise on the low pressure side of the apparatus was measured.

The outgassing was considered to be complete when the rate of gas evolution from the coal into the low pressure side was so low that the pressure build-up over a period of two hours could not be measured on the McLeod gauge. It usually took about two days to reach this stage of outgassing.

Although this criterion was quite stringent, the results of later experiments suggest that it provided no guarantee that outgassing had been completed or that the surface was always cleaned to exactly the same extent in all the experiments. While such a deficiency would affect the results and their reproducibility it was not practicable to continue the outgassing indefinitely.

Reproducibility of measurements

The theoretical accuracy of the method depends on the accuracy of the pressure measurements and in this case should be about one per cent. Actually, measurements of the flow rates of helium were found to be reproducible to within two per cent when doing duplicate determinations on the same disc.

With other gases (that could be absorbed more or less on the coal) the reproducibility was generally not better than 10 per cent. This is probably due to adsorption and desorption effects and to the displacement of gases in the coal not previously removed during outgassing.

Although it was considered impracticable to continue with the outgassing much over 50 h, an effort was made to increase the reliability of the determinations, as far as a coal type was concerned, by doing at least consecutive duplicate runs with any gas on the same disc and by repeating the duplicate experiment with the same gas using a second disc prepared from the same coal lump or core. The average result of these (at least four) experiments was then used in subsequent calculations.

While no claim is made to high accuracy in the results thus obtained, it is considered that they are reliable enough to indicate trends.

Evaluation and discussion of results

Flow characteristics of different gases at constant temperature and pressure—To determine the diffusion characteristics of different gases in coal, extensive

work was done on different plugs of the same coal (B) at 25°C and 40 cm of mercury (water vapour pressure 20 mm). The results in *Table 5* represent the average value obtained for three different plugs and duplicate measurements on the same plug.

Table 5. Permeability coefficients determined from flow rate measurements of coal sample B at 25°C and 40 cm of mercury (water vapour pressure 20 mm of mercury)

Gas	*Flow rate ergs/min* $\times 10^2$	*Total permeability* cm^2/sec $\times 10^{11}$	*Gas permeability* cm^2/sec $\times 10^{11}$	*Surface permeability* cm^2/sec $\times 10^{11}$
H_2	8·1	3·9	3·7	0·2
He	5·4	2·6	2·6	—
CH_4	5·9	2·8	1·3	1·5
H_2O	10·0	4·8	1·2	3·6
N_2	1·8	0·9	0·8	0·1
CO	2·1	1·0	1·0	—
O_2	8·8	4·2	0·9	3·3
CO_2	2·1	1·0	0·8	0·2
Kr	1·1	0·5	0·4	0·1

Adsorption measurements were made on finely crushed coal at the same temperature and pressure to determine the relative affinities of the gases for coal and to evaluate v required for calculating P from equation 2. These results, and other constants of the gases required in the discussion, are given in *Table 6*. The values of the molecular diameter[20] are derived from the van der Waals equation.

Table 6. Molecular constants of the gases studied and the amounts of gas absorbed by 1 g of coal B at 25°C and 40 cm of mercury

Gas	*Molecular diameter*	*Molecular weight*	$PM^{\frac{1}{3}}$ $\times 10^{11}$	*Amount Adsorbed* cm^3
H_2	2·34	2	5·5	0·08
He	2·65	4	5·2	—
CH_4	2·30	16	11·2	7·25
H_2O	2·88	18	20·4	77·0
N_2	3·16	28	4·8	0·41
CO	3·12	28	5·3	0·37
O_2	2·92	32	23·8	13·3
CO_2	3·23	44	6·6	4·1
Kr	3·69	83·8	4·6	3·9

Effect of affinity of gas for coal—It will be observed that with the exception of methane, water vapour and oxygen, surface flow apparently only plays an insignificant role in the diffusion process.

With methane, on the other hand, it is at least as important as the gas phase diffusion and with water and oxygen it is the more important factor. This relatively large surface flow is probably due to the higher affinities of these gases for coal, as indicated by the amounts adsorbed.

With methane, its relatively small molecular diameter probably has an important bearing on its flow and adsorption characteristics. Thus, comparing it with the higher boiling gases krypton and carbon dioxide, one would not expect that more methane should be adsorbed. It is probable that due to their relatively small size, the methane molecules can penetrate pores that are inaccessible to the larger molecules. Although the percentage of pores having diameters of 2 and 3 Å may be low, they would contribute appreciably to the surface area and the surface flow observed with methane may be due to penetration to such surfaces.

Such surfaces would also be available to helium and hydrogen but no surface flow is observed with these gases, probably because of their very low affinity for coal.

Considering the experiments with water vapour, one must expect the large amount of water absorbed to be due largely to capillary condensation in the pores at the high relative pressure at which the adsorption was measured (viz. 0·8). The observed amount adsorbed cannot therefore be regarded as a measure of its affinity for the coal relative to that of the other gases.

However, assuming that the heat of adsorption is of the same order of magnitude as the heat of liquefaction of water, one must conclude that the attractive forces between coal and water are greater than those of any of the other physically adsorbed gases included in this study. Quite apart from any capillary condensation effect, one would expect on this basis that relatively large quantities of water molecules would be adsorbed by coal.

The observed high rate of surface flow of water vapour may therefore be ascribed to the comparatively large number of water molecules that are adsorbed and can move across the surface. The large dipole attraction between water molecules must also have a considerable effect on the flow characteristics of water vapour.

Oxygen is adsorbed in comparatively large quantities by coal at 25°C. At this temperature chemisorption is probably quite appreciable and the forces binding the chemisorbed oxygen molecules may be expected to reduce their mobility. These molecules should also obstruct the flow of the more mobile, physically adsorbed molecules. The observed high rate of surface flow suggests that relatively large quantities of physically adsorbed molecules must be present on the surface, and as a calculation shows that the amount of oxygen adsorbed under the conditions under which the flow measurements were made only covers about 10 per cent of the monolayer capacity of the coal surface, it is clear that enough unoccupied surface area was available for the unhindered flow of mobile oxygen molecules.

Effect of molecular weight of gas—With the gases that are less strongly adsorbed surface diffusion makes only a small contribution to the total observed flow. These gases are therefore transported mainly in the gas phase.

Considering only the gases (helium, hydrogen, carbon monoxide and nitrogen) where the surface flow contributes less than 10 per cent of the total flow, it is found that the observed total permeability varies roughly as

the reciprocal of the square root of the molecular weight. This is the relationship to be expected with molecular streaming and it may be concluded that the flow in the gas phase is mainly governed by a mechanism of the nature of that postulated by Knudsen.

In the fourth column of *Table 6*, the products $PM^{\frac{1}{2}}$ for all the gases are given. It is seen that the gases with higher affinities deviate from the general trend of dependence on the molecular weight probably because of the relatively large contribution of surface diffusion.

The effect of reduction of pore radii on the gas phase diffusion during the course of adsorption cannot be studied by this method but it is likely that it has a considerable influence on the flow characteristics of gases in coal in which the predominant pore sizes are of molecular dimensions.

On the other hand, coal also has pores with dimensions large enough for bulk diffusion to take place. However, the results clearly indicate that this type of flow does not govern the overall diffusion.

Effect of molecular size of diffusing gas—Since molecular streaming and surface flow are dependent on the radii of the pores, it could be expected that the flow would be affected if there were a large number of pores with radii approximating to those of the diffusing gases.

Considering the gases hydrogen, helium, nitrogen and carbon monoxide whose diameters range from 2·3 to 3·2 Å and which are only slightly adsorbed (so that the effect of a variation in pore radii consequent on adsorption is excluded), it is found that the value of $PM^{\frac{1}{2}}$ is fairly constant. This seems to indicate that no molecular sieve effects arise in the gas phase and that there are relatively few pores of these dimensions in coal.

However, since the large surface area of coal is mostly located in these micropores, enhanced surface flow is observed with adsorbed molecules such as methane whose dimensions are such that these surfaces are accessible to them.

Effect of pressure on diffusion—Experiments were conducted at constant temperature and at pressures (Δp) ranging from 2 to 60 cm of mercury. With the gases having a small surface flow such as helium, hydrogen, nitrogen and carbon monoxide the pressure appeared to have no effect on the rate of flow.

With the other gases the results were found to fluctuate so much that it was impossible to establish any trend.

Effect of temperature—The rate of flow of most gases increased only slightly with temperature and due to the difficulty in reproducing results no general relationship could be established.

However, with helium the reproducibility was better and values of the diffusion coefficient calculated from measurements made at 25° and 85°C (on coal B) were found to be $2{\cdot}6 \times 10^{-11}$ and $2{\cdot}8 \times 10^{-11}$ cm²/sec respectively. This represents an increase of about 7·7 per cent over this temperature range whereas dependence on $T^{\frac{1}{2}}$, as required for molecular streaming, would

require an increase of about 9 per cent. Although the agreement cannot be considered to be good, the results indicate that the diffusion of helium is not exponentially dependent on temperature.

A fairly large increase in the flow rate is observed with water vapour and methane in the temperature range 25° to 60°C. The values of the total and surface diffusion coefficients obtained at various temperatures are given in *Table 7*.

Table 7. Effect of temperature on diffusion of methane and water vapour at 40 cm and 2 cm of mercury pressure respectively

Gas	*Total permeability coefficient*	*Activation energy kcal/mol.*	*Surface permeability coefficient*	*Activation energy kcal/mol.*
Temperature, °C	25 38 60		25 38 60	
Methane	2·8 3·1 3·6	2·5	1·5 1·8 2·0	2·8
Water	4·8 5·0 6·0	2·2	3·6 3·8 4·2	1·6

By plotting log P against $1/T$ for the surface permeability coefficients the slopes of the best average straight lines through the points indicate that the activation energy for methane is 2·5 and 2·8 kcal/mol. for the total permeability and surface permeability respectively. For water vapour the values are 2·2 and 1·6 kcal/mol. respectively.

Effect of porosity of coal—The study of the effect of porosity on gas flow is complicated by the fact that surface and gas permeabilities depend on the porosity in different ways.

Table 8. Effect of porosity coal on flow rate of some gases at 25°C and 40 cm of mercury pressure

Gas	*Permeability coefficient* $cm^2/sec \times 10^{11}$		
	Porosities, cm^3/g		
	0·146	0·121	0·085
He	2·9	2·6	2·2
N_2	1·1	0·9	0·8
CO	1·0	1·0	0·8
Kr	0·6	0·5	0·3

According to the theory[16, 17] the gas permeability should decrease rapidly with a decrease in porosity and the surface permeability should increase with decreasing porosity. The net effect will therefore be determined by the relative contribution of the surface and gas flows to the total flow.

Furthermore, if the permeating gas is adsorbed, another complication is introduced by the possible reduction in the pore diameter and porosity in the course of the adsorption process.

In view of these difficulties the flow behaviour of only the slightly adsorbed gases, with which relatively little surface flow and adsorption occur, were studied on three coals of varying porosities. In *Table 8* the values for the total permeabilities are given for coals with porosities ranging from 0·15 to 0·08. With this range of porosities a fourfold variation could be expected. From the results given in *Table 8* no definite relationship can be established although a decrease in the permeability is observed with decreasing porosity.

Comparison between diffusion coefficients obtained by the different methods— To be able to compare the results obtained by the adsorption and flow rate methods it is necessary to convert the permeabilities obtained by the latter method to diffusion coefficients.

The surface diffusion coefficient may be calculated by means of equation 2 and since it is assumed that the gas flow is independent of the surface flow, the gas diffusion coefficient is numercially equal to the gas permeability.

In *Table 9* the values of the total diffusion coefficients obtained for oxygen and water vapour by the two methods are listed. These results indicate a considerable disparity between the values by the different methods.

Table 9. Total diffusion coefficients for oxygen and water vapour

Gas	*Total diffusion coefficients, cm²/sec*	
	Flow rate method	*Adsorption rate method*
Oxygen	$1{\cdot}14 \times 10^{-11}$	$4{\cdot}5 \times 10^{-14}$
Water vapour	$1{\cdot}24 \times 10^{-11}$	$4{\cdot}8 \times 10^{-13}$

With oxygen the flow rate method yields values that are higher by a factor 10^3 and for water, by a factor 10^2. The differences in the experimental conditions, such as the degree of coverage, aggregate-state of the sample and in the case of oxygen, the pressure, cannot account for the large difference in the diffusion coefficients.

It therefore seems probable that the higher flow rate in the solid plug is due to microcracks and fissures which are destroyed when the coal is ground to a finely subdivided state. This flow through cracks etc. may be expected to play an even more important role in larger lumps or even the seam of coal.

CONCLUSIONS

The total diffusion coefficient for a number of gases is of the order of 10^{-13} cm²/sec for powdered coal and 10^{-11} for flow in a solid plug. These values compare favourably with those of Zwietering and Joy who obtained values of 10^{-12} cm²/sec calculated from methane adsorption rates. Graham obtained a value of 10^{-8} for the permeation through a solid slab of coal. From these results it may be concluded that the coal substance is almost impermeable to gases and that the higher permeation rates observed with solid plugs are due to microcracks and fissures in the coal.

A comparatively large surface flow is observed with strongly adsorbed gases such as oxygen and water vapour. The enhanced flow of methane can be ascribed to a higher surface area available to its relatively small molecules. The flow of these gases is activated with activation energies of 2 to 3 kcal/mol.

The flow of less strongly adsorbed gases is probably governed by molecular streaming because it is independent of pressure but is related to the temperature and molecular weight by the expression $(T/M)^{\frac{1}{2}}$. The flow of these gases also increases with porosity.

The diffusion coefficient of water has been found to increase with increased pressure but the oxygen flow seems to be independent of the pressure. The flow characteristics of oxygen are complicated, however, by the fact that it is chemisorbed.

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*The Separability of Pyrite Particles in Some Pulverized Coals**

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The pyrite content was determined in forty one pulverized bituminous coal samples, and in the 'sink' fractions obtained by a density separation in a liquid medium of density 1·450 g/ml. Two of these coal samples were sieved and the different sized fractions were also subjected to pyrite determinations and density separations. The percentages of pyrite, ash and combustible matter which are removed in the 'sink' fractions are presented. The results indicate that much of the pyrite in the coals studied exists as relatively free particles and can be separated from the powdered coal by the float-and-sink method.

THIS laboratory is engaged in a study of the mineral matter in commercially pulverized coals and on its effects upon combustion properties of the coals, upon corrosion and slag deposition in boilers, upon composition and properties of fly ash, and similar problems. As part of this study the present work was undertaken to determine the manner of dispersion of pyrite† and the limiting values for the physical separability of pyrite from the carbonaceous matter.

Forty one samples of pulverized American bituminous coals ranging in total pyrite content from 1·03 to 9·62 per cent were studied. Pyrite and ash determinations were made on each of these samples and on the 'float' fractions obtained from them by density separations. From the resulting data the percentages of the pyrite, ash and combustible material which were removed in the 'sink' fraction were calculated. The analytical methods, referred to below, could not be applied to the 'sink' fractions for direct determinations, because a significant part of the small quantities involved could not be removed from the filter paper.

Two of the coals have been examined in greater detail. Different sized particles obtained by a standard sieve analysis of the pulverized coals were likewise subjected to pyrite determination and density separations; pyrite determinations were also made on each of the 'float' fractions.

EXPERIMENTAL

Coal samples

Two groups of coals from different mines were used. The first group from Pennsylvania and West Virginia is listed in *Table 1*.

These coals were ground in the same commercial ball mill. The particle size distribution of the pulverized samples varies, but for this group an average of about 90 per cent of the sample passes a 100-mesh sieve and nearly 60 per cent passes a 200-mesh sieve.

* Presented before the Division of Gas and Fuel Chemistry of the American Chemical Society, Chicago, Illinois, Meeting, 7–12 September, 1958.
† The word 'pyrite' in this work refers to iron disulphide in the form of pyrite or marcasite.

The second group of samples, identified only as to the states in which the mines were located, was a selection of high-pyrite content coal samples supplied by the U.S. Bureau of Mines*. This group of samples was ground in a laboratory hammer mill. An average of about 88 per cent of a sample passes a 100-mesh sieve, and about 82 per cent passes a 200-mesh sieve.

Table 1. First group of coal samples examined

No.	*Mine*	*Coal Bed*	*State*	*County*
1 + 1a	*Williams*	*Pittsburgh*	*West Virginia*	*Marion*
2 + 2a	*Rich Hill*	*U. and L. Freeport*	*Pennsylvania*	*Cambria*
3	*Arkwright*	*Pittsburgh*	*West Virginia*	*Monongalia*
4	*Purseglove*	*Pittsburgh*	*West Virginia*	*Monongalia*
5	*Rosedale*	*Pittsburgh*	*West Virginia*	*Monongalia*
6 + 6a	*Indian Creek*	*Lower Kittanning*	*Pennsylvania*	*Fayette*
7	*Kano*	*Redstone*	*West Virginia*	*Upshur*
8	*Badger*	*Redstone*	*West Virginia*	*Barbour*
9	*Compass*	*Pittsburgh*	*West Virginia*	*Barbour*
10	*Lynn*	*Pittsburgh*	*West Virginia*	*Monongalia*
11	*Diamond*	*Lower Kittanning*	*Pennsylvania*	*Indiana*
12	*Clymer*	*Lower Kittanning*	*Pennsylvania*	*Indiana*
13	*Ebensburg*	*Lower Kittanning*	*Pennsylvania*	*Cambria*
14 to 16	*Composite samples*		*(Run-of-mill)*	

Sieve fractions

Method *D 197–30*[1] of the American Society for Testing Materials (A.S.T.M.) was used to obtain sieving fractions from two of the pulverized coals. Fractions passing the 325-mesh screen, not mentioned by this procedure, were also prepared (in a similar fashion) because these fractions made up over one third of each of the samples (as received) that were studied in detail.

Density separations

All density separations were made with a carbon tetrachloride–xylene mixture having a density of 1·450 g/ml. Sharper separations were more readily obtainable in this mixture than in others that were tried. At lower densities appreciable quantities of light organic particles appear in the 'sink' fraction while at higher densities there is little change in the amount of 'sink' fraction.

The separations were made as follows: 5 g of pulverized coal was introduced into a 500 ml borosilicate pear-shaped separatory funnel and then 250 ml of the density mixture was added. The funnel was stoppered, shaken well and clamped in a vertical position. After one hour the contents were carefully shaken in such a manner that the upper part of the vessel was well wetted, the floating fraction was thoroughly disturbed, but the heavy fraction was left essentially undisturbed. After one more hour, this procedure was repeated; the funnel was then left untouched until a clear separation was obtained. The bottom 50 ml of fluid and sediment were drawn off and filtered; the weight of the sediment was obtained after drying to constant weight at 100°C. The 'float' fraction was similarly reclaimed quantitatively.

* Through the courtesy of Mr R. F. ABERNETHY and Mr J. J. BURNS, Central Experiment Station, Region V U.S. Bureau of Mines, Pittsburgh, Pa.

Analysis

Pyrite was determined by a modification[2] of R. A. MOTT's method[3] and ash was determined by A.S.T.M. method *D 271–48*[4]. Both were determined in the samples before the density separation and in the 'float' fraction after such a separation. The pyrite and ash in the 'sink' fraction were calculated by difference.

All analyses are averages of at least two replicate determinations.

DISCUSSION

Data for the distribution of the pyrite in the various sieving fractions of the Williams coal (Sample No. 1) and of the Rich Hill coal (Sample No. 2), and in the 'float' and 'sink' fractions derived from these sieving fractions, are presented in *Tables 2* and *3*.

*Table 2. Williams coal (Sample No. 1). Distribution of pyrite in the different fractions, after sieving and density separations**

Fraction size	*% of whole coal*	*Pyrite, % in fraction*	*'Floats' % of fraction*	*Pyrite, % in 'Floats'*	*'Sinks' % of fraction*	*Pyrite, % in 'Sinks'*	*Per cent of pyrite in sieving fraction, appearing in 'Sinks'*	*Per cent of pyrite in whole coal, appearing in 'Sinks'†*
< 325 *mesh*	36·45	0·88	98·04	0·39	1·96	25·4	56·6	11·1
200–325 *mesh*	23·65	1·80	94·33	0·29	5·67	26·9	84·8	22·0
100–200 *mesh*	27·95	2·26	93·00	0·31	7·00	28·1	87·2	33·6
50–100 *mesh*	11·00	2·38	92·50	0·31	7·50	28·1	88·3	14·1
30– 50 *mesh*	1·50	—	—	—	—	—	—	—
16– 30 *mesh*	0·12	—	—	—	—	—	—	—

* In *Tables 2* and *3* all tabulated percentages are expressed on a weight basis.
† These percentages have been computed on the basis of the pyrite percentages found in the whole fractions.

*Table 3. Rich Hill coal (Sample No. 2). Distribution of pyrite in the different fractions, after sieving and density separations**

Fraction size	*% of whole coal*	*Pyrite, % in fraction*	*'Floats' % of fraction*	*Pyrite, % in 'Floats'*	*'Sinks' % of fraction*	*Pyrite, % in 'Sinks'*	*Per cent of pyrite in sieving fraction, appearing in 'Sinks'*	*Per cent of pyrite in whole coal, appearing in 'Sinks'†*
< 325 *mesh*	44·30	1·59	95·53	0·24	4·47	30·39	85·4	29·7
200–325 *mesh*	24·70	1·96	98·24	0·16	11·76	15·49	92·9	22·2
100–200 *mesh*	22·90	2·60	83·14	0·20	16·86	14·44	93·6	27·5
50–100 *mesh*	7·13	3·38	79·32	0·22	20·68	15·53	95·0	11·3
30– 50 *mesh*	0·86	—	—	—	—	—	—	—
16– 30 *mesh*	0·03	—	—	—	—	—	—	—

* See first footnote to *Table 2*.
† See second footnote to *Table 2*.

From these tables it is apparent that each of the four largest sieving fractions contains an appreciable amount of pyrite. These four fractions in the aggregate contain approximately 99 per cent of the original pulverized coal. After density separations, between 56·6 per cent and 95·0 per cent of the pyrite in a sieving fraction is found in the 'sink' fraction. This suggests that a large part of the pyrite in these two powdered coals was present in a comparatively unencumbered state. Only a relatively small part of the total weight of the

pyrite was retained in the 'float' fractions, occluded in or attached to carbonaceous matter. Samples of the 'sink' fractions of these two pulverized coals were embedded in blocks of Lucite, which were then ground and polished. Few pyrite particles, >325 mesh, were found attached to carbonaceous particles; none were found attached to other inorganic materials.

It can be deduced from the data in the last column in *Tables 2* and *3* that the bulk of the pyrite is not present in any one sieving fraction. It is, therefore, not practical to segregate a particular sieving fraction from the pulverized coal for the purpose of removing pyrite, in the case of these two coals.

Computation shows that the sum of the amounts of pyrite that settle in the 'sink' fractions of the sieving fractions equals 81 and 91 per cent of the pyrite content of the original Williams and Rich Hill samples, respectively. Data show that the amount of pyrite that settles in the sink fraction of the whole pulverized coal equals 87 and 90 per cent of the pyrite content of the original Williams and Rich Hill samples, respectively. These data are in good agreement, considering the nature and the number of analyses involved. On the basis of the results of the experiments done on samples No. 1 and No. 2, it was not considered necessary to perform sieving separations on the remainder of the forty one samples.

The separability of pyrite from other whole coal samples was determined by the density separation method described. The data obtained in these separations, as well as the results of pyrite and ash determinations, and derived data, are given in *Tables 4* and *5*.

The data presented may help to form an impression of pyrite and ash removal, and combustible matter loss, that may accompany a density separation of pulverized coal. The frequently considerable variation in properties of samples from one coal bed, and the even greater differences

Table 4. Results of density separations, ash and pyrite determinations. (*First group of coals*)

Sample No.	*Sink loss*, % of coal*	*Pyrite in whole coal, %*	*Pyrite in 'Floats' %*	*Pyrite removal %*	*Ash in whole coal, %*	*Ash in 'Floats' %*	*Ash removal %*	*Combustible loss, %*
1	5·74	1·65	0·22	87	—	—	—	—
1a	5·99	3·20	0·52	85	8·54	4·97	45	2·4
2	9·98	1·78	0·17	91	—	—	—	—
2a	10·18	1·98	0·22	90	10·33	6·85	36	6·7
3	7·24	1·59	0·45	74	—	—	—	—
4	7·07	1·50	0·60	63	—	—	—	—
5	7·49	1·95	0·47	78	—	—	—	—
6	11·88	2·56	0·21	93	—	—	—	—
6a	10·54	2·08	0·24	90	9·34	5·71	46	6·9
7	4·23	1·03	0·30	72	—	—	—	—
8	5·45	1·20	0·39	69	—	—	—	—
9	4·98	2·55	0·51	81	6·68	4·38	38	2·1
10	5·81	2·51	0·49	82	7·07	4·85	35	3·6
11	8·45	3·73	0·84	79	8·66	5·10	46	4·9
12	9·72	2·32	0·64	75	11·08	6·69	45	5·4
13	6·35	1·70	0·43	76	6·05	4·66	28	5·1
14	6·10	2·58	0·43	84	7·30	4·99	36	3·8
15	5·84	2·40	0·47	82	7·48	5·03	37	3·3
16	6·93	3·01	0·49	85	8·20	4·90	44	3·6

* In *Tables 4* and *5* 'sink loss' represents the percentage of the dry powdered coal that sinks in the density fluid. 'Pyrite removal', 'ash removal' and 'combustible loss' express the percentages of the pyrite, ash and combustible contents respectively, of the original sample, found in the heavy fraction ('Sinks') of the density separation. Tabulated percentages are on a weight basis.

between coal samples with different geographic origins, restricts the drawing of specific conclusions.

The percentage of the pyrite that is removed, expressed on the basis of the original pyrite content, varies from 63 to 93 per cent for the coal samples listed in *Table 4*, and from 51 to 82 per cent for the samples listed in *Table 5*.

Table 5. Results of density separations, ash and pyrite determinations. (***Second group of coals, high sulphur content***)

Sample No.	*Location of mine*	*Sink loss*, % of coal*	*Pyrite in whole coal %*	*Pyrite in 'Floats' %*	*Pyrite removal %*	*Ash in whole coal, %*	*Ash in 'Floats' %*	*Ash removal %*	*Combustible loss, %*
20	*Illinois*	8·45	2·32	1·10	52	7·98	4·89	44	5·4
21		8·05	2·04	0·67	70	7·57	5·47	34	5·9
22		9·98	3·26	1·05	71	8·83	5·88	40	7·2
23		9·91	2·68	0·97	67	9·86	6·23	43	6·4
24		8·90	2·51	0·97	65	9·32	6·23	39	5·7
25		9·24	2·51	0·90	67	9·74	6·73	37	6·3
26	*Kentucky*	5·45	2·02	0·92	57	6·53	4·48	35	3·4
27		7·44	2·23	0·92	62	8·00	4·49	48	3·9
28		3·85	2·04	0·99	53	5·26	3·83	30	2·4
29		7·73	2·36	1·05	59	7·87	5·07	41	5·0
30	*Ohio*	6·82	2·56	1·35	51	7·82	5·27	37	4·2
31		7·80	3·03	1·01	69	7·88	5·63	34	5·6
32		21·68	9·62	3·24	74	12·07	5·69	63	16·1
33		17·27	7·82	3·00	68	9·71	5·91	50	13·8
34		12·35	5·20	2·15	64	7·56	4·58	47	9·6
35		11·53	6·40	2·36	69	9·09	5·00	51	7·6
36	*W. Virginia*	7·88	3·41	0·67	82	9·08	5·91	40	4·8
37		6·94	3·18	0·62	82	8·51	5·44	41	3·8
38		12·40	4·83	0·79	86	12·28	6·79	52	7·0
39		10·36	2·36	0·60	77	10·73	7·49	37	7·2
40	*Kansas*	8·24	3·28	1·46	59	10·49	6·08	47	3·8
41		7·59	3·07	1·39	58	9·56	5·66	45	3·6

* See footnote to *Table 4*.

Ash removal percentages vary from 28 to 63 per cent, and combustible matter losses in the sink fractions range from 2·1 to 16·1 per cent.

The various loss and removal data stem from one separation operation. If the 'sink' fraction is subjected to an additional density separation in a fluid of the same density as previously used, a part of the combustible matter can be reclaimed. This was not systematically investigated. In two cases (Samples Nos. 1 and 2) the combustible loss could thus be decreased by 0·7 per cent, however. In these two cases, the limit of separability by physical means had been approached in one density separation.

CONCLUSIONS

(1) On the basis of a detailed study of two samples of commercially pulverized steam coals, it may be expected to be impracticable to segregate any particular sieving fraction from pulverized coal for the purpose of removing pyrite.

(2) The pyrite particles in these coal samples appeared to be present largely as free particles, or as particles that are relatively unencumbered by carbonaceous or inorganic matter.

(3) Part of the pyrite can be removed from pulverized coal by a density fluid. Forty one samples were studied. At a density level of 1·450 g/ml, the

percentage of the total pyrite removal in the 'sink' fraction varied from 51 to 91 per cent. At the same time, the ash content of the pulverized coal was decreased by an amount varying from 28 to 63 per cent. In the process a loss of combustible matter, ranging from 2·1 to 16·1 per cent was encountered.

(4) It was shown in two cases, that the limit of separability by physical means had been approached in one density separation.

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*A Modification of Mott's Method for the Determination of Pyritic Sulphur in Coal**

W. VAN HEES and E. EARLY

Mott's method for the determination of pyritic sulphur in coal is based on acid extractions of two samples of pulverized coal. One sample is extracted with hydrochloric acid, the other with nitric acid. Iron is determined in the extracts. Values thus obtained are used to calculate the pyritic sulphur content of the coal. A labour-saving extraction procedure has been developed, useful when only pyritic sulphur has to be determined.

R. A. MOTT[1] developed a procedure for the determination of sulphate and pyritic sulphur in coal, that is referred to in the literature as the British Coke Research Association method. It is a modification of the method of A. R. POWELL and S. W. PARR[2] in that the extractions take place with dilute boiling acids during one half hour, instead of at room temperature, or at 60°C, for periods up to forty hours. Mott's method is recommended by A. H. EDWARDS, G. N. DAYBELL and W. J. S. PRINGLE[3] when the highest accuracy is required. A short description of Mott's method follows.

Five grammes of coal, ground to pass a No. 70 sieve, are boiled for one half hour with 50 ml of 5N hydrochloric acid in a 500 ml conical flask provided with a reflux condenser. The coal residue is then filtered off and washed. In the combined filtrate and washings, iron and, if desired, sulphate sulphur is determined.

A second sample, of one gramme only, of the minus No. 70 mesh coal, is boiled for one half hour with 50 ml of 2N nitric acid in the manner indicated above. After filtering and washing the residue, iron is determined in the combined filtrate and washings. The percentage iron found by hydrochloric acid extraction ($\%Fe_A$) is subtracted from the percentage found by nitric acid digestion ($\%Fe_B$). The former is non-pyritic in origin, while the latter is pyritic as well as non-pyritic. The concentration of pyritic sulphur is calculated from the proportion

$$\%S_{(pyr.)} = 1{\cdot}148\,(\%Fe_B - \%Fe_A)$$

When it is not necessary or essential to determine sulphate, but only pyritic sulphur, a simplification resulting in the saving of work can be applied.

It is proposed that, in contrast to Mott's 'simultaneous' method, a 'non-simultaneous' procedure be followed. The coal is extracted with hydrochloric

* Presented before the Division of Gas and Fuel Chemistry of the American Chemical Society, Chicago, Illinois, Meeting, 7–12 September 1958.

acid, filtered and washed. The extract is discarded. The residue is quantitatively transferred to the nitric acid, extracted, filtered and washed. The iron in the combined filtrate and washings is determined; it is solely of pyritic origin. The pyritic sulphur is then calculated from the proportion

$$\%S_{(pyr.)} = 1{\cdot}148\,(\%Fe)$$

The present paper presents the comparative results from the analysis of a series of samples of bituminous coals from Pennsylvania and West Virginia, using both methods.

EXPERIMENTAL

Determinations of pyritic sulphur were made in twelve samples by Mott's method. These were followed by determinations made by the 'modified method' according to the following detailed description.

Table 1. Pyritic sulphur content (per cent) of coals by Mott's method and by proposed 'modified method'

Coal	*Mott's method*		*'Modified method'*	
1	0·960 0·911	0·94	0·961 0·969	0·97
2	1·215 1·225	1·22	1·218 1·232	1·23
3	0·814 0·812	0·81	0·813 0·812	0·81
4	0·959 0·965	0·96	1·009 1·024	1·02
5	0·682 0·619	0·65	0·616 0·653	0·63
6	2·176 2·276	2·23	2·281 2·388	2·33
7	0·896 0·861	0·88	0·867 0·874	0·87
8	0·291 0·275	0·28	0·270 0·270	0·27
9	0·915 0·912	0·91	0·924 0·930	0·93
10	1·410 1·644	1·53	1·483 1·476	1·48
11	0·936 0·947	0·94	0·907 0·964	0·94
12	0·879 0·879	0·88	0·873 0·873	0·87

One gramme of coal, powdered to pass a No. 70 sieve (American Society for Testing Materials, *E 11–39*) is boiled for one half hour in a 500 ml conical flask with 50 ml of 5N hydrochloric acid. The flask is provided with a reflux condenser*.

The coal is filtered off and washed with dilute hydrochloric acid (1:20) until the filtrate is free of iron (test with potassium thiocyanate), then a few times

* The use of rubber stoppers (a potential source of sulphur) in acid extraction apparatus is permissible, because only iron is determined.

with distilled water. The filtrate is discarded*. Filter paper and residue are then transferred to a 500 ml conical flask and boiled for one half hour with 50 ml of 2N nitric acid in the manner indicated above. The contents of the flask are filtered and repeatedly washed with 2N nitric acid. The iron in the combined filtrate and washings is determined in one of the usual ways. The procedure used in this work, a titration of Fe^{2+} with Ce^{4+}, is given in detail in standard texts[4, 5].

Table 1 presents results of duplicate determinations and their averages, obtained with Mott's method and with the proposed modification, for the pyritic sulphur contents, for twelve samples of pulverized coal.

DISCUSSION OF RESULTS

It was found that it was sometimes difficult (particularly with having a relatively high pyritic sulphur content) to prepare duplicate samples. Very careful mixing of the samples of powdered coals resulted in the values tabulated. It is likely that the cause of erroneous results was in the inhomogeneous distribution of the larger pyrite particles in the ground coal. It has been shown that these particles are present in association with only a small amount of organic matter[6]. Since they are considerably denser than the organic material in coal, it seems quite possible that pyrite particles may become locally concentrated in the grinding process and during transport and subsequent handling. The frequently considerable inhomogeneity of coal in its natural state is an additional potential source of sampling difficulties.

The standard deviation of the differences between duplicate pairs of determinations from their mean[7] was found to be equal to $\pm 0{\cdot}055\%$ $S_{(pyr.)}$ for Mott's method, and equal to $\pm 0{\cdot}026\%$ $S_{(pyr.)}$ for the 'modified method'.

With Mott's method, the expected uncertainty in the mean of a pair of duplicate determinations will not exceed $\pm 0{\cdot}114\%$ $S_{(pyr.)}$ in 95 per cent of all cases. At the same confidence level, the expected uncertainty in the mean of a pair of duplicate determinations will not exceed $\pm 0{\cdot}055\%$ $S_{(pyr.)}$ for the 'modified method'. On the basis of these calculated values, it may be concluded that the 'modified method' affords greater precision than Mott's method. The 'modified method' is simpler (readings and observations are reduced to 50 per cent of the number necessary for Mott's method). This may in part account for the greater precision of the 'modified method'.

Application of Student's *t* test[8] to the data in *Table 1* shows that there is no significant difference between the mean values obtained for the series of twelve samples by the two methods. Therefore, it may be concluded that there is no significant systematic difference between the two methods.

An additional ninety six pairs of duplicate determinations of pyritic sulphur were made by the 'modified method', using samples from as many different sources. The results of these ninety six sets of duplicate determinations were combined with the twelve sets of determinations previously made by the 'modified method', for statistical treatment. The standard deviation of

* No attempt to determine sulphur in this filtrate should be made since only one gramme of coal is used. A 5 g sample, as recommended by Mott (see ref. 2) for sulphate sulphur determinations, is advisable.

the differences between duplicate pairs of determination from their mean was found to be equal to $\pm 0{\cdot}037\%$ $S_{(pyr.)}$. This represents an expected uncertainty in the mean of a pair of duplicate determinations no greater than $\pm 0{\cdot}074\%$ $S_{(pyr.)}$ at the 95 per cent confidence level.

Although the concentration of pyritic sulphur in these samples did not exceed approximately 2·3 per cent, there is no reason immediately apparent why the conclusions would be different with higher pyritic sulphur concentrations.

CONCLUSION

A modification of Mott's method for the determination of pyritic sulphur in coal has been developed. This modification is labour saving. Statistical treatment of data obtained on a series of coal samples, using both methods, shows that the 'modified method' compares favourably with the existing method.

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*Pyrolysis of Coal I—Thermal Cracking of Phenolformaldehyde Resins Taken as Coal Models**

K. ŌUCHI and H. HONDA

In order to elucidate the thermal cracking of coals, pyrolysis of seven kinds of phenolformaldehyde resins was first examined. The principal gaseous products were methane, water, carbon monoxide and hydrogen. Methane is produced from two sources, methyl radicals and the bridged parts of —CH_2—. The former are decomposed at a lower temperature than the latter. Water is produced from hydroxyl radicals and carbon monoxide from the water produced and the decomposed bridged parts of —CH_2—. Simple calculation shows that about 70 per cent of the carbon atoms in the bridged parts remains in the residual carbon. The greater the percentage of methyl radicals in the sample, the greater is the expected yield of methane, and the less that of carbon monoxide and water. On the other hand, the greater the amount of hydroxyl groups in the sample, the more the yield of water, carbon monoxide and carbon dioxide, and the less that of methane. Differences in condensation type (whether linear, slightly three-dimensional or strongly three-dimensional) have only a small influence on the decomposition.

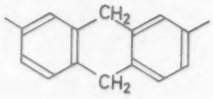
COAL is believed to be a kind of polymer having aromatic ring clusters as base units, the size of the base units increasing with increasing coal rank. Coal begins its decomposition and carbonization at temperatures as low as 300° to 400°C producing gas and a tarry lower molecular weight distillate, formed by the rupture of side chains or relatively weak linkages. The nature of these side chains and linkages plays a very important role in the structure and properties of coals. Coal degradation studies, however, have had limited success in identifying these side chains and linkages owing to the complexity of the coal structure, so the thermal cracking of a series of phenolformaldehyde resins taken as coal models has been studied to elucidate the ease of rupture of side chains and linkages, yields and identity of gases.

In previous papers the authors reported the structure changes of this series of phenolformaldehyde resins in carbonization using specific gravity[1, 6], diamagnetic susceptibility[2, 6], electrical resistance[3, 6], x-ray diffraction[4, 6], and hardness[5] etc. From these studies, the authors concluded that the ease of graphitization of phenolformaldehyde resins depends on the kind of original phenol, namely the greater the number of OH or CH_3 radicals, especially the latter, the greater is the ease of graphitization. It was further concluded that the carbonization process of phenolformaldehyde resins can be subdivided into the following three heating temperature ranges.

(1) *From the decomposition temperature to about 700°C*
In this temperature range the diamagnetic susceptibility suddenly decreases and reaches a minimum at about 700°C. The carbonaceous materials produced

* This research was reported at the 8th Annual Meeting of the Chemical Society of Japan (April, 1957).

in this temperature range have unpaired electrons and no large condensed aromatic rings. The samples having no CH_3 radicals do not show new bridge linkage of the benzene nuclei at all and the samples having CH_3 radicals produce new bridge linkages between their benzene nuclei as follows:



(2) *From about 700° to about 1400°C*
The values of diamagnetic susceptibility[2, 6], electrical conductivity[3, 6] *a* axis crystallite dimension[4, 6], specific gravity[1, 6], and hardness[5] increase beyond 700°C with carbonizing temperature. The first two almost saturate and the last three reach a maximum at about 1000 to 1200°C.

The hydrogen atoms bonded directly to the benzene nuclei begin to split off. Then a condensed aromatic structure and a three-dimensional network among the condensed aromatic rings are produced. In this case, samples having CH_3 radicals are apt to develop condensed aromatic rings and unlikely to develop a three-dimensional network among condensed aromatic rings, because these samples have a great tendency to form a new ring between two neighbours as mentioned above. On the other hand, the samples having no CH_3 radicals are likely to develop a three-dimensional network among the condensed aromatic rings and then the carbons produced tend to form irregular structures such as four-, five- or seven-membered rings. When the carbonizing temperature rises higher, the values of diamagnetic susceptibility, electrical conductivity and *c* axis crystallite dimension are almost constant, but those of the *a* axis crystallite dimension, specific gravity and hardness decrease. In particular, the value of the *a* axis crystallite dimension shows a minimum at about 1400°C because the decomposition of the three-dimensional network structure and the rearrangement of molecules occur in this temperature range.

(3) *From about 1400° to about 2000°C*
In this temperature range, the values of diamagnetic susceptibility, and *a* and *c* axis crystallite dimensions increase suddenly with heating temperature. The carbons produced in this temperature range behave like graphite and have a negative temperature dependence of diamagnetic susceptibility. The value of diamagnetic susceptibility at room temperature increases linearly with that of the *c* axis crystallite dimension above the range of heating temperatures in which the carbon produced shows the negative temperature dependence of diamagentic susceptibility. The carbon produced in this temperature range has large condensed aromatic rings and a two-dimensional graphite-like lattice.

In this step there can be great differences in the growth of the crystallite owing to the variety of phenolformaldehyde resin samples. The samples having many CH_3 radicals show excellent development of crystallite size because CH_3 radicals readily give rise to bridges between neighbouring

aromatic rings. Samples having no CH_3 radicals show the development of crystallite size similar to that of cellulose.

On the basis of these considerations, the gases produced by thermal cracking of seven phenolformaldehyde resins up to about 1000°C have been analysed by their mass spectra.

EXPERIMENTAL PROCEDURE

The apparatus used is shown in *Figure 1*. It comprises the taper-jointed quartz reaction vessel, *A*, of about 20 cm³, the taper-jointed trap, *B*, of about 30 cm³, the desiccator tube, *C*, the mercury manometer, *D*, the gas reservoir,

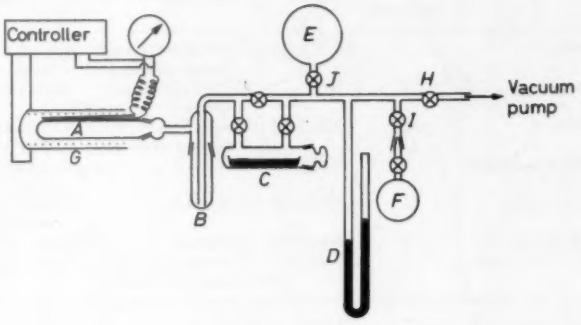


Figure 1. Apparatus

E, of about 2000 cm³ and the taper-jointed gas sampler, *F*, of about 200 cm³. This apparatus is connected to the vacuum system. The reaction vessel is heated to the required temperature by the electric heater, *G*, using the temperature controller.

The phenolformaldehyde resin specimens were pulverized to pass through a 30 and stand on a 60 Tyler mesh sieve and stored in a calcium chloride desiccator. The phenolformaldehyde resins are those which were used in the earlier work[1–5]. The characteristics of these resins are listed in *Table 1*.

At first, for the analysis of the gases produced, the following procedure was used. About 1 g of the dried sample was weighed into the reaction vessel and phosphorus pentoxide was put in the desiccator tube in order to avoid introducing water vapour into the ion source of the mass spectrometer. The experimental apparatus was evacuated to 10^{-5} mm of mercury and the stop cocks, *H*, *I* and *J* in *Figure 1*, were closed; then the reaction vessel was heated. Temperature readings were taken by means of a Pt/Pt–Rh thermocouple. The temperature was raised at 2°C per minute to the final temperature. The pressure of gas evolved was kept below 50 mm of mercury using an evacuated gas reservoir, in order to suppress the secondary decomposition as little as possible. When the temperature had been raised to the desired level, the pressure of gas was read from the mercury manometer and the sample of gas was collected in the evacuated gas sampler. Then the gas sampler was exchanged, the

apparatus evacuated as quickly as possible, and the stop cock *H* was closed. This procedure was repeated at intervals of about 100°C. The gas samples were analysed by means of an R.M.U.-4 mass spectrometer made by Hitachi Ltd, Japan.

Secondly in order to measure the quantity of water and lower molecular weight substance (tarry distillate) produced, the following procedure was carried out. A further 1 g of the same sample was weighed into the reaction

Table 1. Properties of samples used

Sample No.	*Kind of phenols*	*Phenol / Formaline mol ratio*	*Catalyst*	*Form of condensation*	*Characteristic change in heating*
1	*Phenol*	1	NH_4OH	*Three-dimensional (weak network)*	*Almost no change in form of particles*
2	*Phenol*	1	HCl	*One-dimensional (linear)*	*Melt; swelling*
3	*Phenol*	$\frac{1}{2}$	NH_4OH	*Three-dimensional (strong network)*	*No change at all in form of particles*
4	*Hydroquinone*	1	NH_4OH	*Unknown*	*No change at all in form of particles*
5	*Pyrogallol*	1	NH_4OH	*Unknown*	*A little swelling; becoming globular*
6	m-*Cresol*	1	NH_4OH	*Unknown*	*Some adhesion*
7	*1,3,5-Xylenol*	1	NH_4OH	*Unknown, perhaps one-dimensional*	*Melt; swelling*

vessel and evacuated to 10^{-5} mm of mercury without phosphorus pentoxide in the desiccator tube. The trap was immersed in liquid oxygen and then the reaction vessel was heated under continuous evacuation. The temperature was raised at 2°C per minute to the desired level and the stop cock *H* was closed. Thereafter the electric heater was removed and the reaction vessel cooled to room temperature. The stop cock *H* was opened, dried air was introduced into the apparatus, and the liquid oxygen was removed. When the trap had reached room temperature, it was disconnected from the apparatus and washed out as quickly as possible by methylalcohol of known water content. The weight of this methylalcohol was measured, and then the quantity of water in 1 ml of it was titrated with Fischer reagent. The reaction vessel was also disconnected from the apparatus and weighed before and after wiping it, as it was being warmed, with absorbent cotton. Thus the quantity of water produced was determined from the former and the yield of non-volatile lower molecular weight substances (a tarry distillate which condenses as soon as it issues from the furnace), was determined from the latter method. The amounts of water and of lower molecular weight substances of No. 2 were not measured. There was no lower molecular weight substance for No. 3. The changes in weight of the same sample were measured by the thermobalance in an atmosphere of dried nitrogen and at the heating rate of 2°C per minute.

The errors of mass analysis are within one per cent. The errors in the measurement of gas volume produced are also under one per cent. Two series of measurement in No. 6 follow a reasonably smooth curve as seen in *Figure 7*.

RESULTS AND DISCUSSION

Figures 2 to *8* show how the production rate of gases varies as the temperature rises. The longitudinal axis is the volume of gas produced per 1 g of the sample divided by the temperature interval, that is the mean production rate of gas. The temperature of the sample is expressed by the mean temperature of this interval.

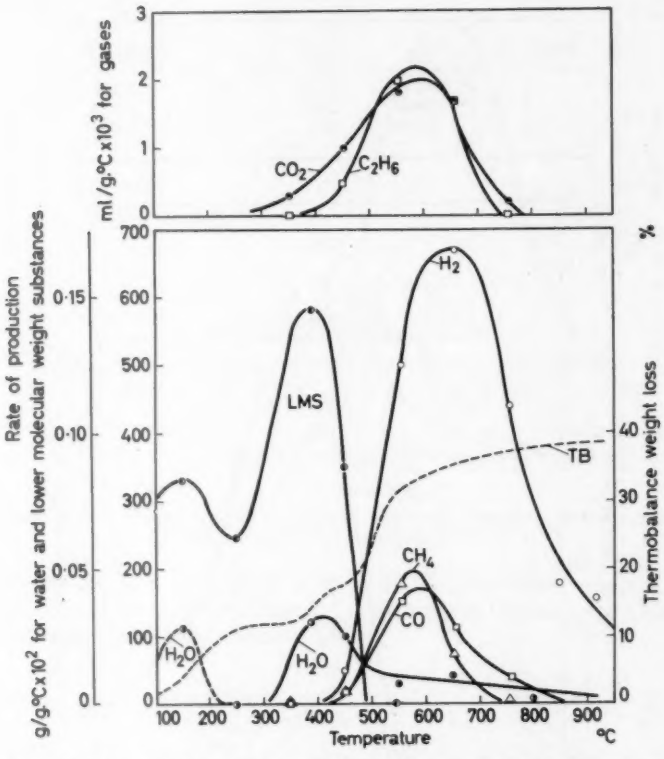


Figure 2. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 1. LMS = lower molecular substances. TB = curve of thermobalance

The experimental results of No. 1 to No. 3 are shown in *Figures 2* to *4*. It is considered that No. 2 has a one-dimensional linear structure, and No. 1 and No. 3 have a three-dimensional network structure; especially in No. 3 the extent of the three-dimensional structure is great. Nevertheless, their decomposition temperature and the temperature of the maximum rate of production of gases completely accord with each other, except that the quantities of the gases produced have some differences. The total volume of gases produced depends upon the quantity of lower molecular weight substances distilled out at lower temperature. The greater the quantity of

lower molecular weight substances, the less becomes the volume of gases produced at the higher temperature. This relation is clear from *Figures 2* to *4* and *Table 2*. The agreement of the decomposition temperature and the maximum rate temperature in No. 1 to No. 3 shows that the thermal cracking of phenolformaldehyde resins is independent of the form of condensation,

Table 2. Total gas volume produced in Nos. 1 to 3 up to 1000°C, ml/g, n.t.p.

Sample No.	H_2	CH_4	CO	CO_2
1	197·0	26·5	30·1	0·30
2	174·0	25·3	18·4	1·30
3	215·0	42·1	37·5	2·61

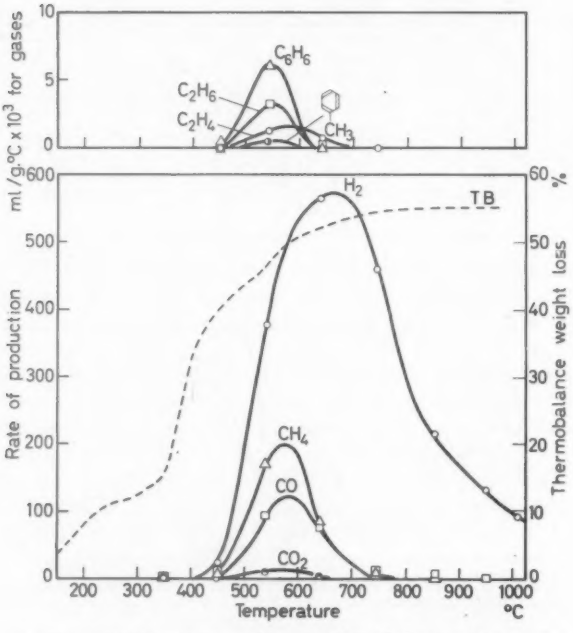


Figure 3. Rate of production of gases and weight loss against temperature for No 2

that is linear or three-dimensional network structure. This is to be expected from the point of view that the thermal cracking of phenolformaldehyde resin takes place at the side chains of OH or the bridges of —CH_2—.

It is almost impossible to deduce the precise mechanism of thermal cracking of phenolformaldehyde resin from these results. But the following mechanism is suggested to account for the kinds of gases produced and the decomposition temperature.

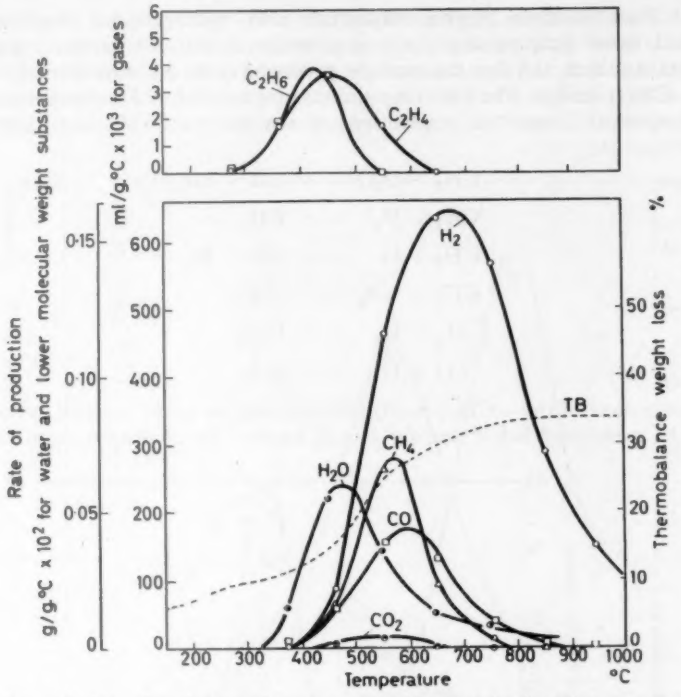
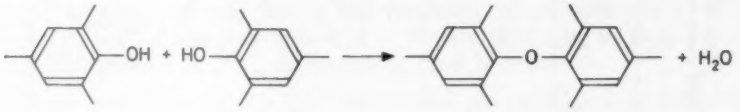


Figure 4. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 3

(*1*) From the fact that water is the first decomposition product, it is understood that the position of the first cracking is at OH radicals. Therefore the following two reactions are considered:



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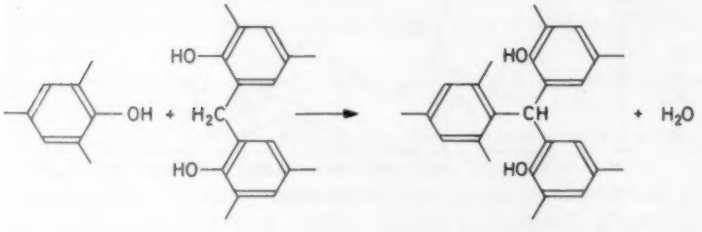


.... [2]

(2) Then methane, carbon monoxide and hydrogen are produced at almost same temperature. As it is considered that the aromatic part is resistant to heat and that the methane produced is the decomposition product of —CH_2— bridges, the following mechanisms are deduced (subject to certain assumptions) from the production of carbon monoxide, methane and hydrogen etc.

$$CH_2 + H_2O \longrightarrow CO + 2H_2 \quad \ldots\ [3]$$

$$CH_2 + H_2 \longrightarrow CH_4 \quad \ldots\ [4]$$

$$CH_2 + O \longrightarrow CO + H_2 \quad \ldots\ [5]$$

$$CH_2 + CH_2 \longrightarrow C_2H_4 \quad \ldots\ [6]$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \quad \ldots\ [7]$$

$$CO + O \longrightarrow CO_2 \quad \ldots\ [8]$$

Because most of the —CH_2— bridged bonds remain in the residual carbon as will be mentioned below and (as is well known) the hydrogen atom of this

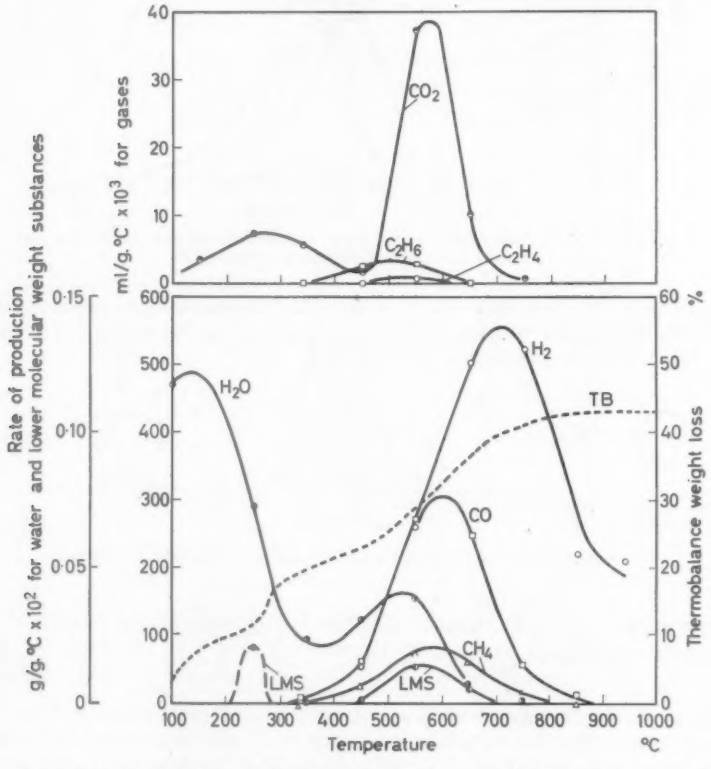


Figure 5. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 4

bridged part is apt to come off in thermal cracking, it is probable that these hydrogen atoms contribute to the hydrogen produced and to reaction 4. It is assumed that the oxygen atom in equations 5 and 8 is produced by the decomposition of the ether linkage formed in reaction 1. It is supposed that reactions 3 and 4 take place much more frequently than the others. This

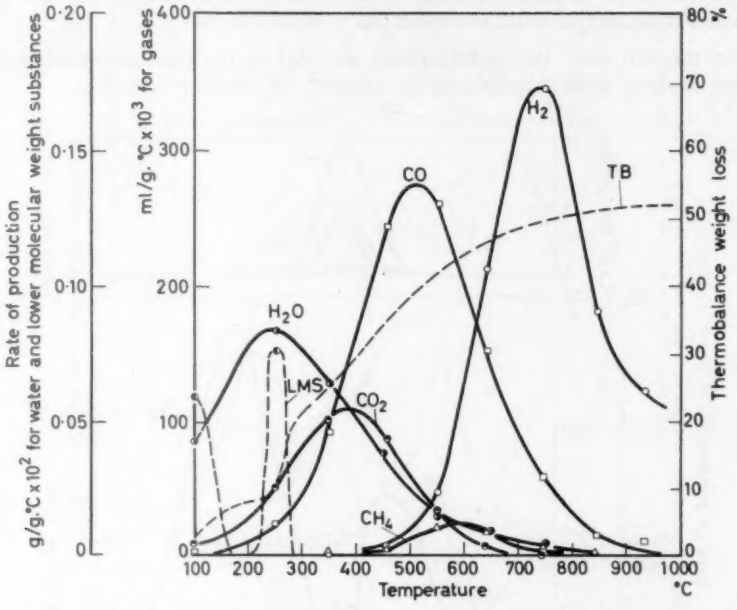


Figure 6. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 5

result suggests that methane is not produced by decomposition of the aromatic part. If the decomposition of the aromatic part takes place, it is natural that more C_2 to C_5 hydrocarbons must be produced.

These deductions of reaction mechanism are considered to be further supported by the following experimental facts:

(*a*) the initial temperature of production of methane, carbon monoxide and hydrogen nearly coincides with the temperature of maximum production of water,

(*b*) the temperature of maximum production of methane almost coincides with that of carbon monoxide,

(*c*) the quantity of ethane, propane, ethylene and propylene etc. increases in proportion to that of methane (see samples Nos. 6 and 7),

(*d*) in sample No. 3 which has the strong three-dimensional structure, namely the many bridged parts of —CH_2—, the production ratio of methane and carbon monoxide to hydrogen is the greatest.

(*3*) At higher temperatures, the hydrogen atoms directly bonded to the benzene nuclei begin to split off[1–3, 6] in the form of H_2. Consequently the temperature of maximum production of hydrogen is the highest of those of the gases produced.

From the above mentioned consideration on the three stages of gas production, the structural change of the residual carbonaceous material of phenolformaldehyde resin is considered to be as follows.

In the first step, the carbonaceous material of the phenolformaldehyde resin contains such structures as the products of equations 1 and 2.

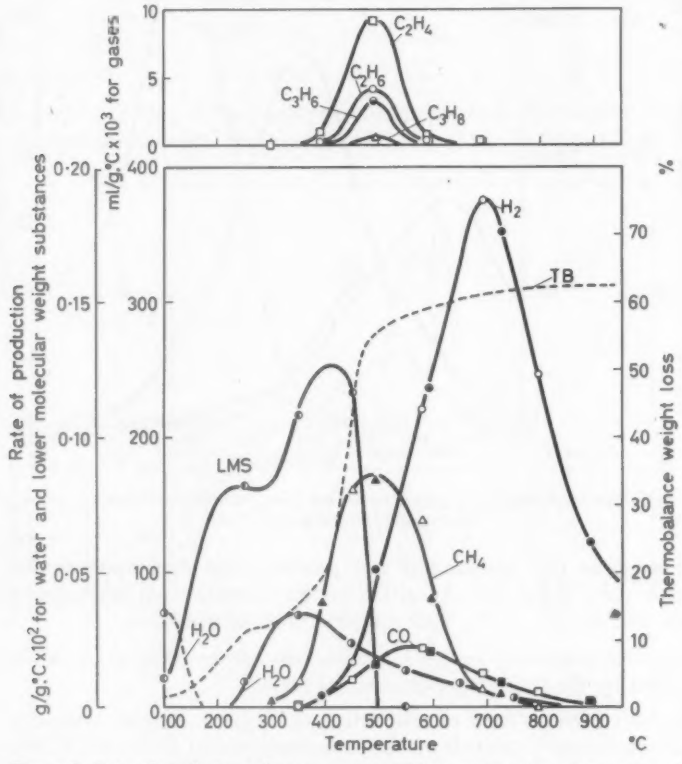


Figure 7. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 6

In the second step, the benzene nuclei combine directly with one another as diphenyl, by the breaking of —CH_2— bridges and —O— bridges. A speculative model of a structure in this stage is given in *Figure 9*. In this step, the decomposition of bridges producing some unpaired electrons and the direct bonding of benzene nuclei take place simultaneously. That is to say, because the resonance system becomes a higher molecular one, some of the free

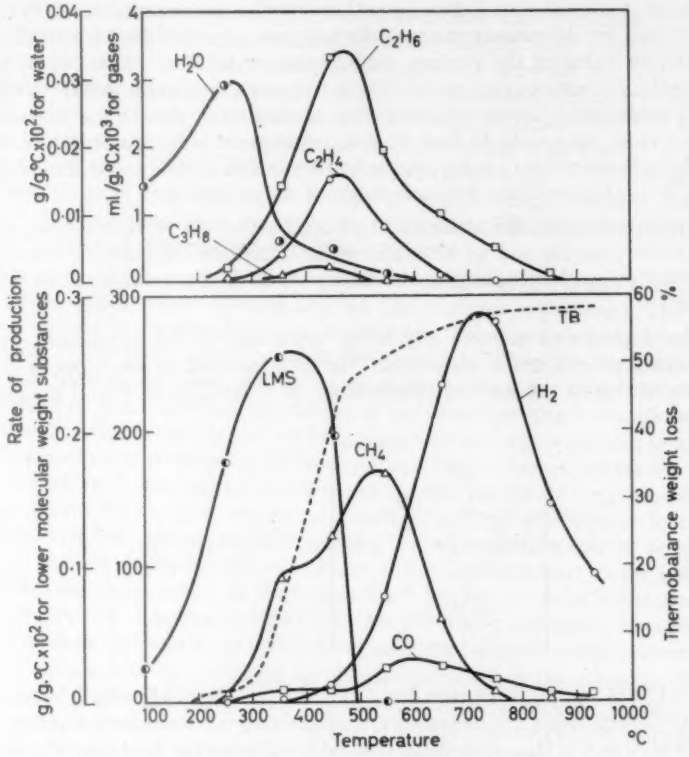


Figure 8. Rate of production of gases, water and lower molecular substances, and weight loss against temperature for No. 7

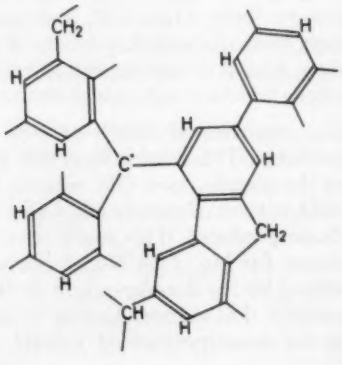
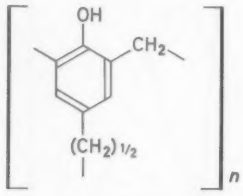


Figure 9. Model of residual hydrocarbon in the second carbonization step

radicals produced in the decomposition reaction become stable. This fact is confirmed by the measurement of diamagnetic susceptibility[2] which shows a minimum value at the heating temperature of 600° to 700°C, or by paramagnetic resonance absorption[7–16] which shows a maximum at 500° to 600°C. This temperature agrees well with that of maximum production of methane and carbon monoxide. In fact, in this temperature range the structure of the carbonaceous product is too strong to permit free rotation and the temperature is too low to cause rearrangement of the molecule.

In the third step, the remaining hydrogen atoms are removed as H_2 and at the same time the size of aromatic nuclei increases suddenly by the partial rearrangement accompanying the strong three-dimensional bonding among them.

No. 3 produces scarcely any lower molecular weight substances, so the following calculation is performed. The total amount of gases per base unit produced up to the heating temperature of 1000°C from No. 3 having the form of



$= [C_{7.5}H_6O]_n$

are 1·1 mol for H_2, 0·19 mol for CO, 0·21 mol for CH_4 and 0·89 mol for H_2O. Consequently the composition of residual hydrocarbon at 1000°C is calculated as $C_{7.1}H_{1.2}$. This value coincides well with the $C_7H_{1.4}$ of elementary analysis. The calculated value of volatile matter is 25 per cent and it accords well with the 24 per cent experimental value obtained by means of the thermobalance. In this case the value of gravimetric measurement is corrected for the decrease up to 300°C because the experiment of gas analysis is carried out for the sample preheated at 300°C in a vacuum. Assuming n is 5, the number of $—CH_2—$ bridges is 7·5. Accordingly the number of $—CH_2—$ bridges splitting to form CO and CH_4 is one each, and 5·5 bridges remain in the residual carbon, that is, about 70 per cent of the bridged part moves to the residual carbon. This is a very important result in contrast with the general view of pyrolysis in which only the aromatic part remains in the carbon.

The experimental results of Nos. 4 and 5 appear in *Figures 5* and *6* respectively. These resins have two and three OH radicals respectively. The more the samples have OH radicals, the greater are the quantities of carbon dioxide, carbon monoxide and water produced, and the less is the quantity of methane produced. This result is to be expected from consideration of the reactions for No. 1 to No. 3 above, because the large amounts of water produced by the decomposition of OH radicals consume CH_2 radicals. It is considered that carbon dioxide produced at lower temperatures is derived from the decomposition of COOH radicals formed by oxidation in air in

the period of hardening of the resins, and that water released at lower temperatures contains that occluded in the sample. The temperature of production of methane and hydrogen is almost the same for No. 1 to No. 3. But the temperature of production of carbon monoxide and carbon dioxide shifts to lower values as the number of OH radicals increases. For No. 4 there are two maxima in the production of carbon dioxide which occur at about 300°C and about 600°C. The former is the decomposition of COOH radicals formed through oxidation in air and the latter is the same for other samples. No. 5 does not show these two maxima. The cause of this is probably attributable to the fact that measured points are few.

The experimental results of Nos. 6 and 7 are shown in *Figures 7* and *8* respectively. These resins have one and two CH_3 radicals respectively. The more CH_3 radicals the samples have, the less become their degrees of condensation, because of the steric hindrance with CH_3 radicals. Therefore the more CH_3 radicals the samples have, the higher are yields of the lower molecular weight distillates or decomposition products and the lower the total volume of gases produced. The temperature at which gas production begins and the temperature of maximum production of hydrogen and carbon monoxide are the same for Nos. 1 to 3, but the total volume of carbon monoxide decreases as the number of CH_3 radicals increases. The total volume of methane increases rapidly, and the temperature of beginning of gas production and the temperature of maximum production of methane shift to lower values, as the number of CH_3 radicals increases. In particular No. 7 has two maxima in the production of methane. The production of carbon monoxide and water decreases in No. 7 because the number of OH radicals contained in the 1 g sample decreases.

The presence of two maxima in the production and the decrease of the maximum production temperature of methane are explained as follows. The production of methane at lower temperatures is due to the decomposition of CH_3 radicals and that at higher temperatures is due to decomposition of $-CH_2-$ bridges as in Nos. 1 to 3. Consequently it is considered that the following reactions take place in addition to reactions 3 to 8:

$$CH_3 + \tfrac{1}{2}H_2 \longrightarrow CH_4 \quad \ldots\ldots [9]$$

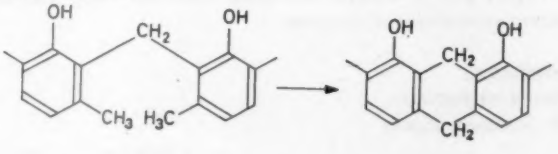
$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad \ldots\ldots [10]$$

$$C_2H_6 + CH_2 \longrightarrow C_3H_8 \quad \ldots\ldots [11]$$

etc.

It is seen that the decomposition of CH_3 radicals begins at about 300°C. In No. 6 these two maxima overlap and the production of methane shows one apparent maximum.

In the pyrolysis of these samples as already pointed out, it is certain that not all CH_3 radicals produce methane or carbon monoxide but the following reactions take place:



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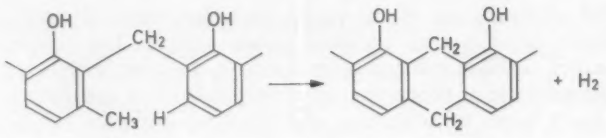

.... [13]

Consequently production of condensed aromatic rings progresses smoothly, while production of the three-dimensional network structure and the disordered structure such as a five- or seven-membered ring in the aromatic nuclei are retarded above 700°C. Moreover these processes promote the growth of a two-dimensional graphite-like lattice beyond 1400°C. As a result of reactions such as 12 and 13, the volume of methane produced at lower temperatures is less than that produced at higher temperatures, though the number of CH_3 radicals is larger than that of $—CH_2—$ bridges in No. 7.

As mentioned above, the aspect of production of gases with changes of heating temperature varies regularly in proportion to the introduction of OH radicals or CH_3 radicals to phenolformaldehyde resin No. 1. The main decomposition temperature of samples in a nitrogen atmosphere by means of the thermobalance does not always correspond to the decomposition temperature of this experiment, especially in samples having proportionately more lower molecular weight substances. This discrepancy may be attributed to the fact that the lower molecular weight substances are distilled off at lower temperatures because the thermal cracking of samples in this experiment is carried out in a high vacuum. It is not clear whether the lower molecular weight substances are products of the thermal cracking of the resins or distillates of the lower condensation substances included in the resins from the outset. Further work is expected to resolve this difficulty.

All samples except Nos. 6 and 7 produce *cyclo*pentadiene above 700°C, though this is not shown in the graphs. It is considered that these samples are more liable to produce a disordered structure in the aromatic nuclei than the samples having CH_3 radicals, therefore the carbonaceous substances of these samples contain the five-membered ring structure. It may be that *cyclo*pentadiene is a decomposition product of the above mentioned disordered structure containing five-membered rings. It is supposed that this disordered structure in the aromatic nuclei disturbs the smooth growth of two-dimensional graphite-like layers up to about 3000°C

The authors wish to thank Messrs K. Egi, N. Mochida, T. Yamakawa, S. Toyoda, Y. Hirose and Y. Sanada who gave them much help and advice in the course of many stimulating discussions.

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The Structure of Coke Oven Tar

E. W. VOLKMANN

Properties of a non-filtered tar and of the corresponding filtered tar indicate that the tar-insoluble phase is not 'inert' material but interacts with the matrix. This interaction is to be expected because X-ray diffraction data show that the tar-insoluble phase is similar to the pitch matrix. A statistical analysis of the constitution of the matrix confirms that, on the average, pitch is made up of low-molecular-weight constituents. Most of the molecules contain not more than 7 nor less than 3 condensed aromatic rings. The behaviour of pitch like a solid is explained by the existence of association forces. They decrease as temperature increases.

IN THIS study of the structure of coal tar, information is obtained by correlations between the physical properties of high-temperature coal tars, or coal-tar pitches derived from them, and some reference substances. High-temperature coke-oven tars or pitches are actually so uniform that they may be regarded as one class of materials. By way of illustration, there are listed in *Table 1* analytical data for a number of pitches made from coke-oven tars of the United States, England, Holland, France, Western Germany, Eastern Germany and of Japan. These pitches contain from 90·8 to 93·2 per cent carbon, and from 3·9 to 5·1 per cent hydrogen. Values of the atomic hydrogen-to-carbon ratio, as listed at the bottom of the tabulation, fall within the relatively narrow range of 0·51 to 0·66 although pitches of varying melting points are included in the tabulation. That pitches derived from such a variety of coals resemble each other so closely, indicates that the high temperature of carbonization is a more important factor in tar formation than the composition and structure of the coal from which the tars are obtained. The close similarity of the analytical data justifies consideration of high-temperature coal tar and coal-tar pitches as one class of materials.

It might be argued that the distillation procedures used for making pitch out of tar are accompanied by deep-seated changes in structure and that, therefore, the two materials must be considered separately. Obviously, this is not so. The distillation of tar with its removal of low-molecular-weight constituents, results in some changes as will be seen from the results of an X-ray examination of the two materials. But these changes are minor, and in general pitch can be considered to be the backbone of tar[9]. For this reason, many tables and charts depicting pitch properties will be presented to illustrate the structure of tar.

Many tar technologists adhere rigidly to the viewpoint that tars are colloidal systems[10–12] because of their peculiar flow properties. Others have come to the conviction that little is gained by emphasizing the heterogeneous nature of the material[5, 13]; they prefer to stress the glasslike nature of the material and emphasize the presence of the great number of constituents, most of which have freezing temperatures far above room temperature. Furthermore, some point out that, with the exception of the tar-insoluble phase, all of the constituents have molecular weights well below 1 000.

Table 1. Analytical data for coal tar pitches

Description	*Pitches used in production of reactor graphite*	*Filtered pitch No. 2 'Koppers Co., Inc.'*	*Quinoline-soluble pitch 'Great Lakes Carbon Corp.'*	*Pitch listed in* D. W. VAN KREVELEN'S Coal Science	*Pitch used by* G. R. BOREHAM *and* R. H. J. HAMMETT	*Pitch studied by* H. G. FRANCK	*Pitch studied by* H. G. SCHÄFER	*Pitch studied by* G. HUGEL	*Pitch studied by* Y. KOSAKA *and* S. KIKKAWA
Literature reference	(1)		(2)	(3)	(4)	(5)	(6)	(7)	(8)
Country	*U.S.A.*	*U.S.A.*	*U.S.A.*	*Holland*	*England*	*W. Germany*	*E. Germany*	*France*	*Japan*
Ultimate analysis									
Carbon, per cent by wt	91·3 *to* 92·9	93·24	91·6	91·7	90·8	92·1	91·7	92·0	90·8
Hydrogen, per cent by wt	4·47 *to* 4·80	4·78	4·64	4·8	4·7	4·5	4·22	5·1	3·91
Nitrogen, per cent by wt	0·81 *to* 1·07	1·10		1·4	0·8	1·3	} 0·8	1·3	0·74
Sulphur, per cent by wt	0·42 *to* 0·53	0·55		0·8	0·9	0·8		0·48	0·83
Oxygen, per cent by wt	—	0·68		2·0				1·1	3·61
Ash, per cent by weight	0·30 *to* 0·10	0·4			0·4		0·28		0·11
Softening point °C	100 (*C/A*)	52·3 (*R & B*)	93 (*C/A*)	40 *Arnu*	75 (*R & B*)	70 (*K & S*)	69 (*K & S*)		101 (*C/A*)
Quinoline insol., per cent by wt	9 *to* 16	0·1	0·1						
Density at 25°C	1·31	1·260	1·269	1·27	—	—	—	—	1·305
Atomic H/C *ratio*		0·61	0·60	0·62	0·62	0·58	0·55	0·66	0·51

NATURE OF THE DISPERSED PHASE

That coal tar is a heterogeneous system becomes immediately apparent when one looks at a thin smear of tar through a microscope and observes against the brown background of the continuous oily matrix innumerable dark particles, most of which are smaller than three microns. The smallest visible ones are perhaps 0·5 micron in diameter and vibrate with the motions of Brownian movement. The dispersed phase amounts to anywhere between 3 and 15 per cent of the tar and is often used to indicate whether in its formation a tar has been exposed to light or severe cracking conditions.

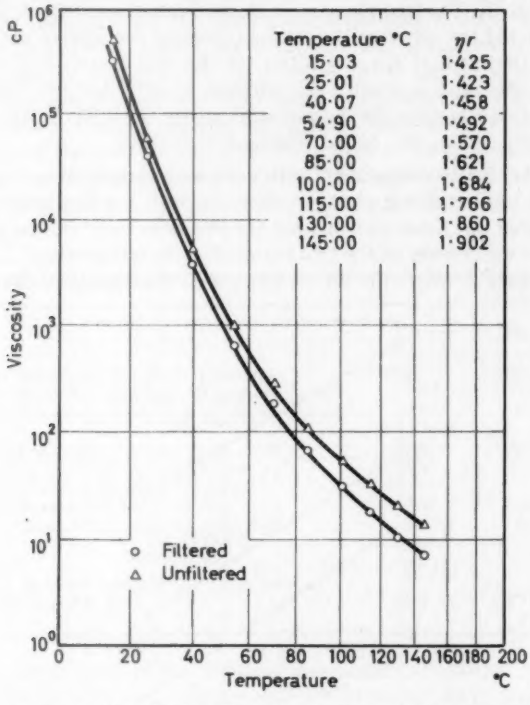

Figure 1. Andrade plot of log *viscosity versus 1/T for a typical coke oven tar*

The question whether the lower limit of the particle size reaches into the ultra-microscopic range could not readily be answered until recently when the development of the electron microscope made possible a study of the fine structure of many materials. A. K. SARKAR[14], using an electron microscope, found that the particles of the dispersed phase of coke oven tars have the approximate dimensions of 2 microns by 1 micron. He comments that 'in the case of horizontal-retort and coke-oven tars, the particles or micelles are comparatively large and their density, defined as number of particles per unit area, is relatively low'. This is in agreement with an earlier publication of

E. J. DICKINSON[15] who adds, however, that in the ultra-microscopic range the photographs of at least low-aromatic tars show a well-defined and regularly dispersed particle structure, the particles themselves having diffuse perimeters and a visible diameter of about 300 Å.

From the practical standpoint it is probably sufficient to consider the dispersed phase, or as the trade calls it 'Carbon 1' or 'C-1', inert material serving the function of a filler. A detailed examination of the situation, however, does not support this view. A viscosity analysis of a typical coke-oven tar and its filtered counterpart demonstrates this, as seen from *Figure 1*. Here the logarithm of viscosity in centipoises is plotted against the reciprocal temperature in °K. The triangles denote the individual viscosity determinations for the unfiltered tar, whereas the circles represent the filtered tar. Inspection reveals that the ratio of the viscosities for the two materials varies. At low temperature this ratio is about 1·42, whereas at 145° it is 1·9. That the ratio changes consistently over the temperature range is shown in the tabulation of the viscosity ratios, also called 'Relative viscosities'.

A rise in the 'Relative viscosity' with increase in temperature indicates that the original, unfiltered tar changes viscosity with temperature less quickly than the filtered tar. Some explanation for this behaviour can be gained from the change of the density of the two materials with temperature. This relation is given in *Figure 2*, where the lowest line shows the density of the dehydrated

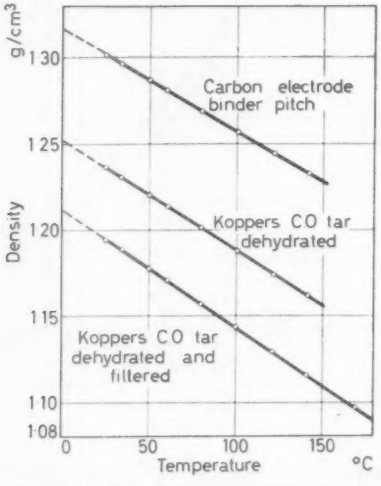

Figure 2. Density versus temperature for typical coke-oven tar and electrode-binder pitch

and filtered tar, whereas the next higher one gives the density for the same tar containing the dispersed phase. From this plot and from the concentration of the dispersed phase, the density of the dispersed phase can be calculated by assuming that by adding the volume of the dispersed phase to that of the filtered tar, the volume of the total tar is obtained. This was done for two

temperatures, namely for 20°C and for 150°C. Surprisingly the density for both temperatures was found to be numerically identical, namely 1·628. The fact that the density remained the same and did not decrease with temperature indicates that the volume of the total tar cannot be calculated from the volume of the two phases. In all probability, some of the molecules originally adsorbed at the surface of the solid particles, went into solution on heating, changing the density of the oily medium and imparting to it substances of relatively high viscosity while leaving behind particles somewhat smaller and denser than they were before the heating-up process.

More rigorous proof for the solution of some of the dispersed phase on heating was obtained from two distillation experiments. 0·5 l. samples of two tars were each placed in a flask and distilled under atmospheric pressure to a softening point of about 70°C. As a measure of the dispersed phase, the quinoline-insoluble portion was determined in the tars as well as in the corresponding pitches. Special caution was used in recovering from the flask the dispersed phase that is often found on the bottom of the flask after distillations of this type. The results are shown in *Table 2*. About one eighth of the dispersed phase originally present in the tars went into solution in the course of the distillations.

Table 2. Disappearance of quinoline-insoluble in laboratory distillations

	Tar 1	Tar 2
Total tar charged to flask; grammes	507	505·3
C-1; *quinoline-insoluble; per cent of dry tar*	1·87	1·61
C-1; *quinoline-insoluble; grammes in dry tar*	9·48	8·14
Softening point of pitch, °C (R + B)	67·0	70·5
Yield of pitch, per cent of dry tar	66·4	57·1
C-1; *quinoline-insoluble; grammes*		
(a) *in pitch poured from flask*	7·92	6·84
(b) *in quinoline washings from flask*	0·51	0·24
Total	8·43	7·08
C-1; *quinoline-insoluble; in pitch, per cent of that found in tar*	88·9	87·0

The solution of some of the so-called C-1 particles in hot tar has, of course, been long recognized. S. J. GREEN and B. THAKUR[16] have studied this and other phenomena of the so-called free-carbon fractions of coal tar, although they have been concerned mostly with tars other than coke oven tars.

Some further insight into the shape and behaviour of the dispersed particles was gained when the 'Relative viscosity' was plotted against the concentration of the solid phase in the tar. The results of this study are given in *Figure 3*, where again two distinctly separate curves are obtained depending upon the temperature of the measurements. The two curves converge at the vertical axis and intersect at unity because with no dispersed phase present, the 'Relative viscosity' must be one. It is interesting to note that the tangent to the lower curve, at the intersection with the vertical axis, forms an angle with the horizontal which corresponds to the 2·5 factor given in the Einstein

equation which expresses the increase in viscosity due to the presence of a suspended phase of spheres. From this it can be deduced that the suspended particles have the general shape of spheres and that they exert no influence on each other at relatively high dilutions. With increased concentration, on the other hand, interaction becomes apparent between particles or between particles and matrix, otherwise the curves for the 'Relative viscosity' would not deviate from the tangent straight lines. Furthermore, the distinctly different curves for 25°C, and for 100°C, indicate temperature dependence of these interactions.

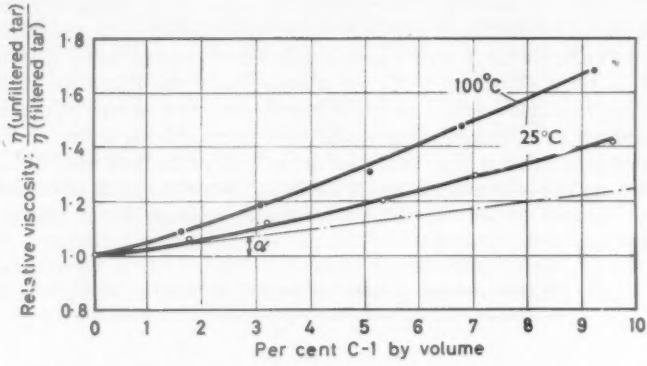

Figure 3. Effect of suspended phase on viscosity for two temperatures

An analysis by x-ray diffraction of the dispersed phase, after separation by filtration, shows the material to be of the same type of compounds that are present in the oily medium of coal tar. Considerations to be discussed later indicate that its molecular weight is between 800 and 1 500.

As a final clue to the nature of the dispersed phase, a tabulation of ultimate analyses, as published by a number of investigators, is shown in *Table 3.* Inspection of the data indicates that the material is not as uniform as coal-tar pitch itself. One reason for the greater spread in chemical constitution is the presence of a large portion of the inorganic material present in coal tar. The variations in hydrogen-to-carbon ratios may also be due to the effects of efforts of differing severity to wash the samples dry of adhering substances. It is likely that prolonged washing will remove successive layers of adsorbed compounds and will leave behind a residue of relatively high molecular weight and of low hydrogen-to-carbon ratio.

NATURE OF THE OILY PHASE

The oily phase is by far the major portion of coal tar. Over 300 individual constituents have actually been identified in the oily phase and it has been suspected that as many as 10 000 constituents may actually be present[5]. Most of these constituents are aromatic hydrocarbons with some heterocyclic ring compounds of the aromatic type. Their total boiling range is about 80° to 550°C for the tar and 350° to 550°C for pitch. In the lower boiling ranges

Table 3. Analyses of quinoline-, or pyridine- insoluble material in coal tar or coal-tar pitch

Treatment	*Pyridine precipitate removed from pitch by*	*Pyridine precipitate removed from tar by*	*Quinoline precipitate removed from pitch by*	*Quinoline precipitate removed from tar by*	*Pyridine precipitate removed from pitch by*	*Dispersed phase removed by centrifuge from tar†*	*Dispersed phase removed by filtration from tar*
Investigator	H. G. FRANCK	H. MALLISON	*Great Lakes Carbon*	*Koppers Co., Inc.*	V. N. KRYLOV	S. J. GREEN *and* B. THAKUR	*Koppers Co., Inc.*
Reference	(5)	(17)	(2)		(18)	(16)	
Ultimate analyses							
Carbon, per cent by wt	92·3	93·4	92·9	93·0	91·54	92·9	
Hydrogen, per cent by wt	3·0	2·6	1·8	2·0	3·58	1·77	
Nitrogen, per cent by wt	0·8	0·65	0·8	0·97	} 0·32	0·9	
Sulphur, per cent by wt	1·0	0·6	0·43	0·71		1·47	
Oxygen (by diff.)	2·4	2·30	0·83	2·80	3·25	1·98	
Ash, per cent by wt		0·45	1·35	0·52	1·31	0·91	
Spec. gravity 25°/25°C			1·65	1·57			1·63*
Atomic H/C *ratio*	0·387	0·332	0·231	0·256	0·466	0·227	

* Calculated from specific gravities of non-filtered and filtered tars.
† Vertical retort tar.

there are still found some alkyl side groups, in particular methyl groups, which are attached to the aromatic ring structures. The higher the molecular weight, the less frequent are the alkyl side chains. Several investigators[5, 6] have reported that no more alkyl groups are found among the constituents boiling above 410°C.

STATISTICAL STUDIES

With such a large number of constituents being present in tar, it becomes a practical necessity to focus attention on the structure of pitch and to consider its make-up from a statistical viewpoint. One requirement in such a statistical study is the selection of a common denominator for comparing aromatic hydrocarbons on the basis of their physical properties. D. W. VAN KREVELEN and J. SCHUYER[19], who have used this approach in their studies of the structure of coal, made use of certain additive functions, i.e. physical properties which may be calculated by summation of atomic contributions within the molecule.

As one important property in these studies, van Krevelen and Schuyer have used 'molar volume' which according to J. TRAUBE[20] can be calculated from the volumes of the individual atoms of a molecule with a correction term expressing structural characteristics. Because of such a relation, it is possible to plot the molar volumes of a homologous series of hydrocarbons against the number of carbon or hydrogen atoms of each member, and to obtain a straight line relationship. Such a plot is well known for the series of paraffinic hydrocarbons. Construction of such a plot involves knowledge of the molecular weights, which are not known with certainty in the case of pitches. Encountering the same difficulty with coal, van Krevelen and Schuyer used, instead of molar volume, the molar volume per carbon atom and related it to the ratio of hydrogen-to-carbon atoms. Following their suggestions but proceeding somewhat more empirically, a diagram was prepared of the simple aromatic hydrocarbons of condensed-ring structure (see *Figure 4*).

When Traube called attention to the additive relationship of molar volume, he was referring to liquids and glasses but not to solid crystalline substances. The aromatic hydrocarbons found in pitches are crystalline substances at room temperature. Hence, it seemed more practical, although scientifically not as sound, to base the diagram on the properties of the aromatic hydrocarbons at 20°C which means using the molar volumes of their solid state. Even this approach could not be strict, because benzene, the parent substance of all aromatic hydrocarbons is a liquid at 20°C. To make it fit into the scheme, it was considered a solid having a density calculated from that of liquid benzene at 20°C by correcting for its contraction at the freezing point.

Returning to *Figure 4*, the diagram is fixed by such key substances as benzene (No. 1), naphthalene (No. 7), anthracene (No. 9) and graphite (No. 6). A line connecting benzene and graphite seems to limit the region of the non-alkylated aromatic hydrocarbons in one direction, while a line connecting benzene with naphthalene and anthracene appears to be another boundary. The first line represents the series of what may be called globularly condensed aromatic hydrocarbons. In its vicinity there are phenanthrene, fluoranthene, pyrene, coronene, and circumanthracene. The second line stands for what

German investigators[6] described as the series of kata-condensed compounds. In its vicinity there are found naphthalene, fluorene, anthracene and naphthacene.

Since some of the low-boiling constituents of pitch contain alkyl side chains, it was of interest to include in the diagram some points for alkylated aromatic hydrocarbons. Because the more highly alkylated aromatics are liquids and not solids, the same approach was taken as for benzene, and a density was calculated for each of the hypothetically solid substances.

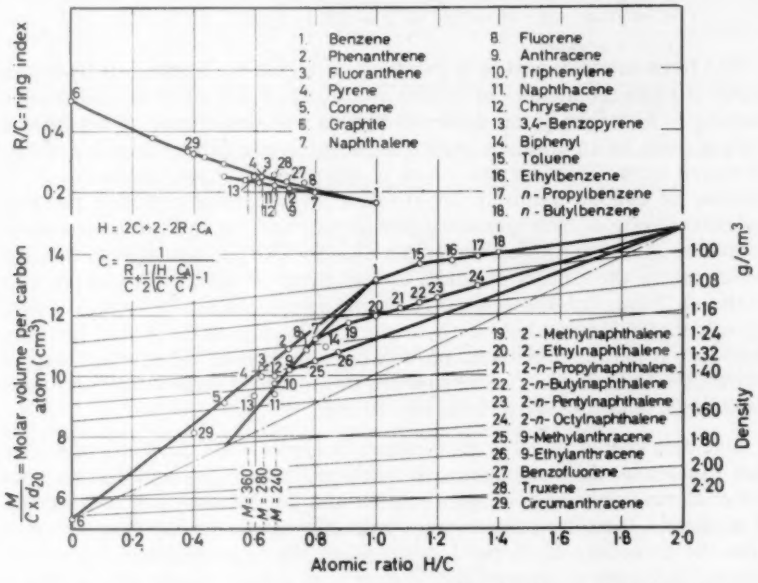

Figure 4. Molar volume per carbon atom versus H/C *ratio of aromatic hydrocarbons*

Points 15, 16, 17 and 18 represent toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene. Points 19, 20, 21 and 22 are the corresponding alkylated naphthalenes, and 25 and 26, alkylated anthracenes. If the points representing each alkyl series are connected and extrapolated, the resulting lines intersect at the abscissa representing an atomic hydrogen-to-carbon ratio of 2·0. This corresponds to polyethylene. It is noteworthy that the density of the point of intersection is 0·95. This happens to be the density of so-called low-pressure polyethylene.

In the upper-left corner of *Figure 4*, D. W. VAN KREVELEN and J. SCHUYER's ring index[21] is plotted as a function of the atomic hydrogen-to-carbon ratio for each of the aromatic non-alkylated hydrocarbons shown on the diagram below. This ring index is the ratio of the number of rings to the number of carbon atoms in the molecule. On the basis of the resulting points, two well defined lines were drawn; the upper curved one represents the globularly condensed, and the lower straight one the so-called kata-condensed aromatic

hydrocarbons. Three points, Nos. 8, 27 and 28, fall above the curved line and even there the deviation is minor. These points represent fluorene, benzofluorene and truxene. Their non-conformance is doubtless due to the presence of five-membered rings.

The significance of the ring index was pointed out by D. W. VAN KREVELEN and his co-workers[22]. They derived the following simple relationship between the number of hydrogen and carbon atoms in an organic hydrocarbon molecule, provided the molecule does not contain truly olefinic linkages

$$H = 2C + 2 - 2R - C_A$$

The formula states that in a paraffinic molecule the number of hydrogen atoms is twice the number of carbon atoms plus 2; for each ring closure the number of hydrogen atoms decreases by two, and substitution of a saturated carbon atom by an aromatic carbon atom involves a further decrease of one hydrogen atom. This formula can be re-arranged to permit evaluation of the number of carbon atoms in an aromatic hydrocarbon provided the ring index, the ratio of hydrogen-to-carbon atoms, and the ratio of aromatic-to-total-carbon atoms are known. It can also be used to estimate aromaticity, which means the ratio of aromatic carbon atoms to total carbon atoms of a molecule. However, the limitation of the formula must be kept in mind, namely that it does not hold for hydrocarbons having simple olefinic linkages, nor does it permit differentiation between the number of aromatic and of naphthenic rings. For pitches derived from high-temperature tars, these limitations are probably without significance.

One difficulty of utilizing the diagram in *Figure 4* for the study of pitches has to do with their containing, in addition to hydrogen and carbon, such other atoms as nitrogen, oxygen, sulphur and the inorganic ash constituents. Fortunately, these other atoms are present in relatively small concentration so that the procedure developed for correcting the experimentally determined atomic hydrogen-to-carbon ratio of pitches to a ratio comparable to that of aromatic hydrocarbons seems adequate for the purpose. Furthermore, the procedure was used only for characterization of filtered pitches or precipitated pitch fractions which do not contain the suspended phase with its relatively high concentration of ash.

In analogy to D. W. VAN KREVELEN and J. SCHUYER's suggestions[23], the correction of the actual hydrogen-to-carbon ratios was based on lifting the oxygen, nitrogen and sulphur atoms out of the molecule and on substituting carbon atoms for them. Hydrogen atoms are added wherever the substitution by carbon atoms has resulted in some residual unsaturated carbon linkages. The details of the procedure are shown in *Table 4* which also indicates the assumed linkages for O, N and S.

To be consistent the density of the tars or pitches should also have been corrected for the substitution of carbon atoms. To do this, various procedures were tried but no reliable method was discovered. Hence, it was decided to use the density of the individual pitches or pitch fractions themselves realizing that a minor error was introduced.

Table 4. Procedure for calculating corrected H/C *ratio from ultimate analysis of pitch*

Element of pitch analysis	Assumed structure	Corrective measure
Oxygen	25% present as: −OH	Removal of this O does not affect H/C ratio
	75% present as: −O−	Replace by C and add 2H
Nitrogen	40% present as: HN	Replace N by C and add one H
	60% present as: N	Replace N by C and add one H
Sulphur	100% present as: S	Replace S by C and add 2H

Formula for calculating corrected H/C ratio:

$$\left(\frac{H}{C}\right)_{corr} = \frac{\frac{\%H}{1{\cdot}008} + 2 \times \frac{0{\cdot}75 \times \%O}{16{\cdot}00} + \frac{\%N}{14{\cdot}008} + 2 \times \frac{\%S}{32{\cdot}06}}{\frac{\%C}{12{\cdot}01} + \frac{0{\cdot}75 \times \%O}{16{\cdot}00} + \frac{\%N}{14{\cdot}008} + \frac{\%S}{32{\cdot}06}}$$

Figure 5 is an enlargement of a portion of the diagram shown in *Figure 4*. For the selected region, this enlargement shows the same aromatic hydrocarbons. In addition, there are shown nine crossed circles representing pitch fractions and three filled circles representing filtered pitches.

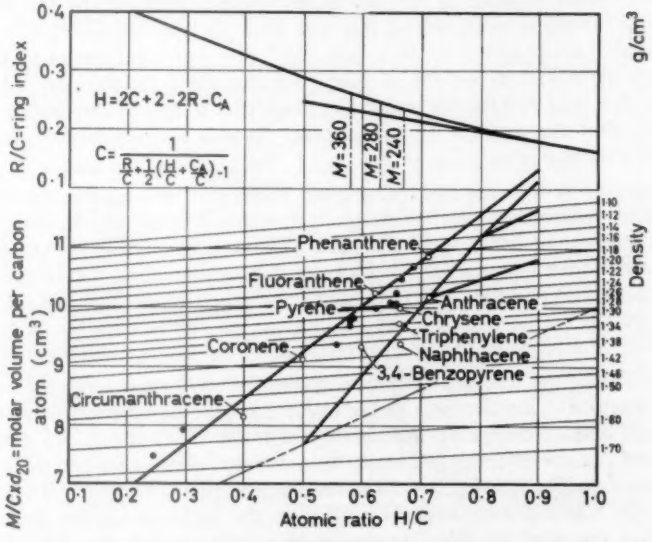

Figure 5. Molar volume per carbon atom versus H/C *ratio of pitches and pitch fractions*

The two crossed circles having hydrogen-to-carbon ratios between 0·2 and 0·3 represent tar-insoluble material separated by filtration and washed until the washing medium did not discolour any longer when in contact with the filter cake. Why these two points fall above the straight line connecting benzene with graphite is not known. Perhaps molecules of the washing medium remained adsorbed to the surface of the material affecting its density. The lower of the two points represents the suspended phase removed from a 'Standard Commercial Pitch Binder' described in the literature[2]. The density for this material was corrected for temperature, and for the presence of ash which was assumed to have a density of 3·0. The other point of atomic ratio about 0·2 represents the suspended phase of a steel-plant tar separated and washed over a prolonged period of time with quinoline until the filtrate no longer showed colour. The curve in the upper portion of the diagram permits an estimation of the average number of carbon atoms per molecule and, hence, of the molecular weights of the two samples provided the materials consisted entirely of aromatic carbon atoms. With this assumption it was found that the suspended phase of the 'Standard Commercial Pitch Binder' contained about 100 carbon atoms and the other material about 70 carbon atoms. This means an average molecular weight of approximately 1 250 for the first, and of 800 for the second case.

The three dashed lines at the upper portion of the diagram marked $M =$ 360, 280 and 240 represent the corrected hydrogen-to-carbon ratios for three pitch fractions described in the German literature[5], together with their molecular weights. Unfortunately the published data do not include the densities of these fractions. With the knowledge of the molecular weights of the three pitch fractions, their aromaticities, i.e. the ratio of aromatic carbon atoms to total number of carbon atoms, were calculated for the average molecule. Depending on which line was used for the determination of the ring index, aromaticities of 96·1 and 101·7 per cent were obtained for the fraction of molecular weight of 360; 96·5 and 100·5 for that of 280; and, finally, 96·1 and 99·3 for the fraction of molecular weight of 240. These values confirm that the average pitch molecule consists almost entirely of truly aromatic carbon atoms.

Returning now to the remaining pitch fractions[22], it is interesting to note that their hydrogen-to-carbon ratios fall within a relatively narrow range. Judging from the location of the pure hydrocarbons, the lowest molecular weight pitch fraction appears to have an average molecule containing more than three, but certainly less than four, condensed rings. The highest molecular weight fraction on the other hand can be represented by an average molecule of more than five, but certainly less than seven, condensed rings.

Calculating the number of carbon atoms for the lowest molecular weight pitch fraction from the ring index curve for globularly condensed hydrocarbons, and assuming an aromaticity of 0·98, 15 atoms or 3·5 rings are obtained for the average molecule. The corresponding data for the highest molecular weight fraction are 24 carbon atoms or 6·5 rings for the average molecule. These results coincide well with the make-up of the three pitch fractions reported by the German investigator[5], as follows. The decalin-soluble portion (molecular weight 240) was listed as consisting of 3-, 4- and

5-membered rings; the xylene-soluble portion (molecular weight 280) of 4-, 5- and 6-membered rings; and the pyridine-soluble portion of 6- and 7-membered rings. The good agreement reached by the two approaches confirms that the molecular weight distribution of the bulk of the components of pitch is narrow.

The three solid points representing the filtered total pitches fall where one would expect them after having observed the location of the various pitch fractions. The one of hydrogen-to-carbon ratio of 0·623 represents a pitch of a melting point of 52·3°C, whereas the other two are carbon-electrode-binder pitches with softening points around 100°C. All three points are relatively close to the line connecting benzene with graphite, which means that their constituents are predominantly globularly condensed. The location of the pitch points also indicates that very few, if any, alkyl side chains are present. Otherwise the pitch points would have appeared in a shift to the right.

Finally, it should be noted that all pitches and pitch fractions, with the exception of the dispersed phase, fall well within the boundaries of the area occupied by the crystalline aromatic condensed-ring hydrocarbons. This could not be anticipated because pitch is a glasslike substance of supercooled liquid components. Therefore, individual molecules must be packed in some regular arrangement for the pitch to have a density as high as that of many of its constituents in crystalline form.

X-RAY STUDIES

To determine whether relatively flat molecules are present in pitch in 'Turbostratic structure'[24] several samples of tar, pitch, pitch fractions and pitch coke were submitted to x-ray examination. The results of this examination are shown in *Figure 6* where the relatively intensity of x-ray diffraction is plotted

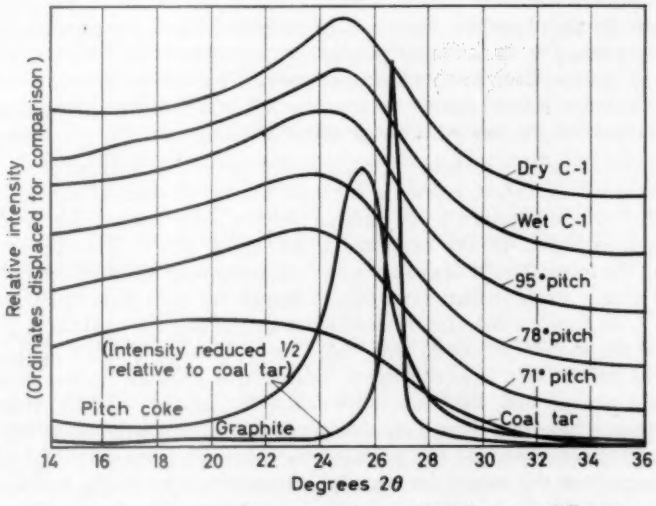

Figure 6. Analysis of coal tar and coal tar residuals by X-ray diffraction

against the diffraction angle. The analysis was performed on a variety of coal-tar materials, starting with a dehydrated coal tar followed by pitches of increasing softening points, by a sample of the suspended phase in the tar, and concluding with the analysis of pitch coke. The coal tar seems to have a relatively flat shape with a bump which signifies infrequent clusters with distances of 5·5 Å between molecules. As the lower boiling constituents are removed from the tar, the orderly arrangement of molecules becomes more frequent. This is indicated by the shape of the curves which assume a more pronounced and definite hump as the melting point is increased. In quantitative terms, this means that more frequently there is alignment with spacings of 4·5 Å between molecules for a pitch of 95° melting point. The distance decreases further in going to the dry sample of the suspended phase. Here it is only 4·3 Å. Finally, pitch coke has a spacing of only 4·24 Å. These spacing values were calculated by the methods described by H. P. KLUG and L. E. ALEXANDER[25] while assuming that the materials show only infrequent, non-crystalline alignment. For comparison there is shown the corresponding x-ray diffraction pattern for graphite which is plotted with an intensity scale only half that of coal tar so as to show the distinct peak. Obviously, graphite consists of layers of lamellae and is arranged in a crystalline pattern. For that reason it shows the pronounced peak. The layers of graphite atoms have a distance of 3·35 Å, a value that the coal tar materials seem to approach as they are further and further distilled.

VISCOSITY STUDIES

Information about the forces which hold these clusters together was gained by the determination of some viscosity properites of pitches[26] and particularly by a study of the viscosity characteristics of a typical coke-oven tar carried out by H. RAICH[27].

That pitches resemble normal liquids obeying the law of Newtonian flow is shown by the diagram, *Figure 7*. In it, rate of shear is plotted against shearing stress for six different pitches having viscosities between 1·5 and $5{\cdot}6 \times 10^7$ poises. Each pitch was tested under five different shearing stresses. When the experimental points were connected, straight lines resulted which on extrapolation intersected at the origin of the diagram.

Many relationships have been proposed for the rate of change of viscosity with temperature. Most resemble the well known Arrhenius equation and state that viscosity equals a constant A times 'e', the base of the system of natural logarithms, to the exponential power of Q/RT. This means that plotting the logarithm of viscosity versus the reciprocal absolute temperature should give a straight line. That this is not so for coal tars was shown in *Figure 1*. In *Figure 8* the viscosity/temperature relation for coal tar is plotted again in the same way, along with those for a number of other substances. As far as may be seen from this figure, simple hydrocarbons such as *n*-hexane do give a straight line. Even methanol and water, in spite of their tendencies for hydrogen bonding, show a reasonable straight-line relationship. The lines representing coke-oven tar and pitch, on the other hand, are definitely curved. For comparison the curves for tricresyl phosphate and for glycerin are also shown.

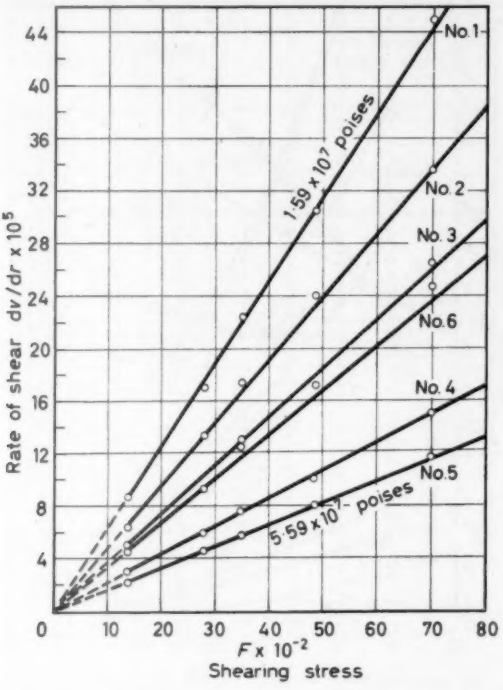

Figure 7. Shearing stress versus rate of shear for several pitches

For an interpretation of the significance of deviations from the straight-line relation, it is advantageous to use S. GLASSTONE, K. J. LAIDLER and H. EYRING's viscosity concepts[28]. They developed a theory of viscous flow which is based on the concept that the elementary process in flow consists of the movement of a single molecule from an equilibrium position into an adjacent 'hole', to occupy another equilibrium condition. The jump from one equilibrium position to the next is treated mathematically as any other rate process involving a chemical reaction and leads to the Arrhenius-type relation between viscosity and temperature. In the Glasstone–Laidler–Eyring form, however, the equation is written

$$\eta = (Nh/V) \exp (\Delta F/RT) \quad \ldots . [1]$$

where η = viscosity in poises, N = Avogadro's number, h = Planck's constant, V = molecular volume, ΔF = free energy of activation for flow, R = gas constant, and T = absolute temperature in °K.

In this form, the constant A of the Arrhenius equation is a definite function of the molecular volume and the exponent assumes thermodynamic significance. With knowledge of the relation between viscosity and temperature, the free energy of activation for flow can be calculated.

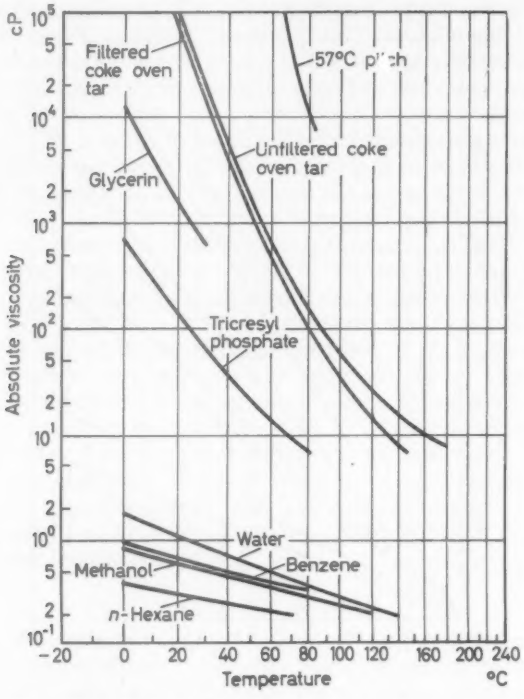

Figure 8. Andrade plot for some associated and unassociated substances

By substituting in the exponent for ΔF the term $\Delta H - T\Delta S$, equation 1 can also be written

$$\eta = (Nh/V) \exp(-\Delta S/R) \exp(\Delta H/RT) \quad \ldots\ [2]$$

where ΔH = enthalpy of activation for flow, and ΔS = entropy of activation for flow.

If ΔS is assumed to be constant over narrow temperature intervals, equation 2 can be differentiated and solved for ΔH to read

$$\Delta H = R\{\mathrm{d} \ln \eta/\mathrm{d}(1/T)\} \quad \ldots\ [3]$$

From this expression, values for ΔH can be calculated by making the approximation

$$\Delta H = R\{\Delta \ln \eta/\Delta(1/T)\} \quad \ldots\ [4]$$

Using these relationships, Raich calculated free energy, enthalpy and entropy of activation for flow as a function of temperature for a typical coke-oven tar. The results of his calculations are shown in *Figure 9*. Because of the uncertainty of the molecular weight of the tar, free-energy and entropy changes were calculated for number-average molecular weights of 200 and

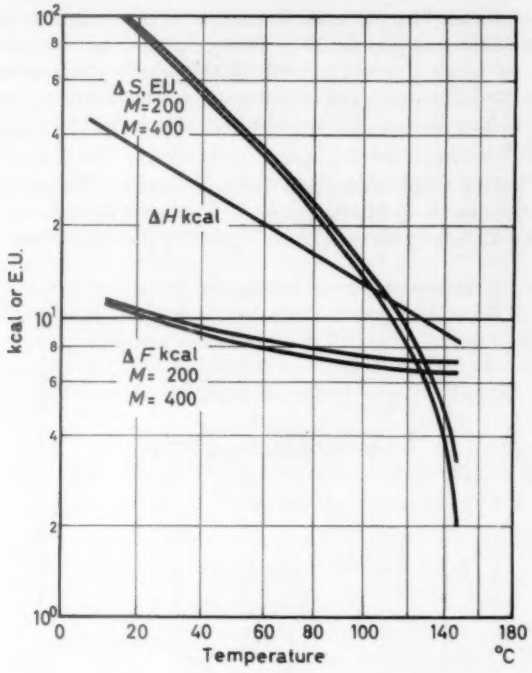

Figure 9. Activation for flow versus 1/T for coke oven tar

400. As may be seen from the resulting double lines, the error introduced by the molecular-weight uncertainty is insignificant.

It is noteworthy that the logarithm of enthalpy of activation changes in a straight-line relationship with the reciprocal of absolute temperature, just as with unassociated liquids, the logarithm of viscosity changes in a straight-line relationship with the reciprocal of absolute temperature. In the highly associated system of coal tar, viscosity changes not only in accordance with the exponential power of enthalpy over *RT*, but enthalpy, in turn, will change with the exponential power of a constant over *RT*.

The relatively large value for the enthalpy of activation and its rapid decrease as temperature is increased can be attributed to the necessity of supplying, in addition to the energy required to form a hole in the liquid, sufficient energy to break association bonds before the activated state for flow can be attained. Since the degree of association decreases as the temperature is raised, the additional 'structural activation energy' diminishes. This leads to the pronounced curvature of the relationship of the logarithm of viscosity versus the reciprocal absolute temperature, the slope decreasing with increasing temperature.

There are two interesting relations which Glasstone *et al.*[28] derived from their theory of viscosity. For liquids obeying the laws of Newtonian

flow, they postulated that the ratio of energy of vaporization to free energy of activation of flow should be 2·45. Using for coal tar a molar energy of vaporization at room temperature of 23 000 calories per gramme mole[28], and the calculated free energy of activation for flow of about 10 000 calories per gramme mole, a ratio of 2·3 was obtained which is close to the 2·45 listed for viscous flow.

A second relation stipulates that for unassociated liquids the ratio of energy of vaporization to the enthalpy of activation for flow equals a value between 3 and 4. As can be seen from *Figure 10*, the value for coal tars does

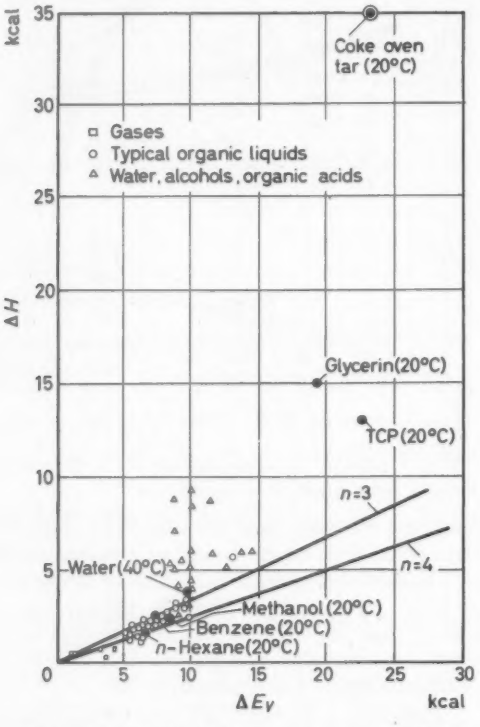

Figure 10. Relationship between energy of activation for viscous flow and energy of vaporization

not fit this relationship and, therefore, suggests the presence of associated clusters.

For comparison, the positions of glycerin and tricresyl phosphate (TCP), both at 20°C, are also shown in *Figure 10*. Glycerin, in particular, is known for its molecular associations due to hydrogen bonding. It is also located considerably above the area limited by the two lines marked $n = 3$, and $n = 4$.

The deviation of coke oven tar from the area of unassociated liquids is

great. This must mean that the degree of association of the coal-tar molecules is unusually high, and is responsible for the strong cohesive forces between otherwise low molecular weight substances.

It is interesting to speculate how large the association forces are. From Raich's calculations, the total enthalpy of activation for flow is about 35 kcal at 20°C; 12 kcal at 100°C; and about 8 kcal per mole at 150°C. According to the postulate of Glasstone *et al.*, the energy of activation for flow with unassociated liquids is about one third to one fourth of the energy of vaporization. This means a hypothetical energy of activation for unassociated tar at 20°C of about 7 kcal; of about 6 at 100°C; and of 5 at 150°C. This leaves for the association forces 28 kcal at 20°C; 6 kcal at 100°C, and 3 kcal at 150°C. For comparison, the dissociation energy required to rupture the aliphatic carbon-to-carbon bond is 60 to 70 kcal, the forces holding water molecules together by hydrogen bonding amount to 11·3 kcal and the molecular cohesion per 5 Å chain length of polystyrene is 4·0 kcal.

DISTILLATION STUDIES

That there are strong forces between coal-tar molecules, even at higher temperatures, became apparent unexpectedly in a study of flash-distillation

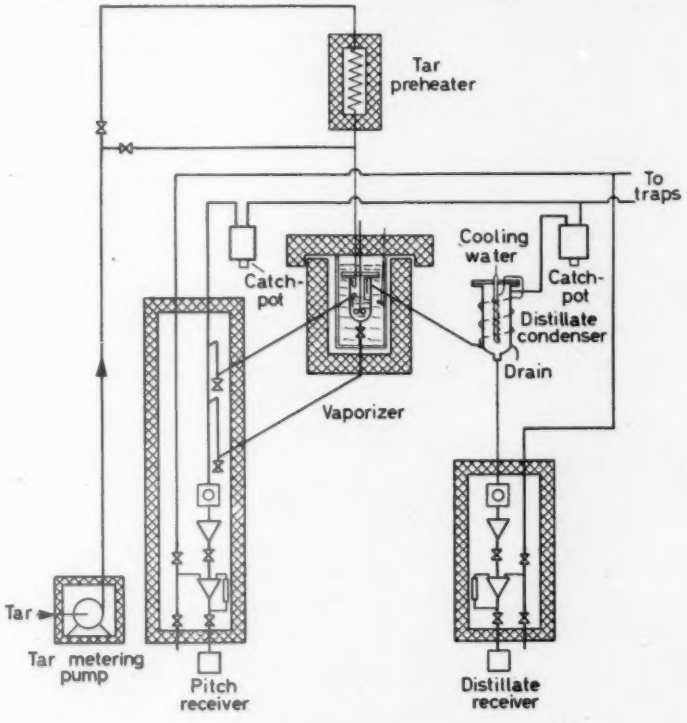

Figure 11. Tar flash vaporization bench unit

characteristics of a number of tars. This study was initiated to determine at what temperatures cracking of some coal-tar constituents would occur with the resultant formation of gaseous or residual byproducts at the expense of distillate yield. The equipment set-up for this investigation is shown in *Figure 11.*

Dehydrated tar was conveyed continuously by a metering pump through a pre-heating coil into a vaporizer consisting of a cylindrical vessel of about 1 gallon capacity, provided with a stirrer. This vessel was surrounded in its entirety by a bath of molten metal maintained at a pre-determined constant temperature. Inside the vessel there was maintained a heel of pitch of constant volume by an overflow arrangement which permitted pitch accumulation to drain into the pitch receivers. The tar distillate passed through a baffle system in the top of the vessel to a condenser from where condensate drained into distillate receivers. The heat of vaporization was supplied by the electrically heated metal bath. The heating surface was ample in size so that the temperature difference between metal bath and pitch was always less than 3°C.

With this equipment, tests were run on the same tar under different pressure conditions. In each case the temperature was adjusted so that the pitch residue had the same Ring-and-Ball softening point. *Figure 12* shows some of the results obtained. With coke-oven tar No. 1, a distillate yield of about 22 per cent was obtained when flash-distilling under a vacuum to a pitch of about 50°C softening point. As the pressure was increased, while

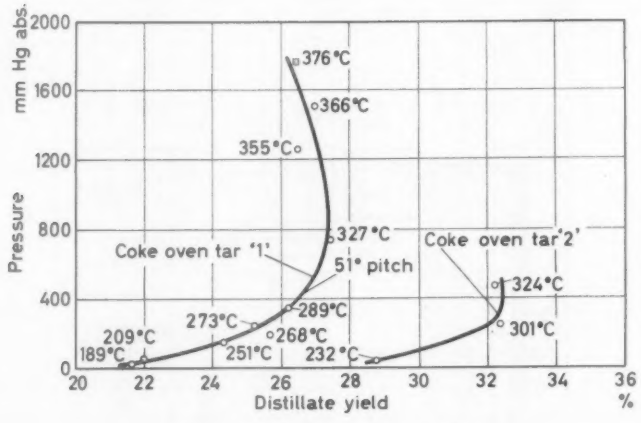

Figure 12. Flash vaporization yields

maintaining the same softening point of the residue, the distillate yield also increased until a maximum yield of over 27 per cent was obtained at atmospheric pressure. Further increase in pressure brought about a slight decrease probably because of the cracking and condensation reactions which constituted the original objective of the investigations.

Obviously, it is not the pressure which should be made accountable for the unusual shape of the distillate curve, but the temperatures which correspond to the selected pressures. *Figure 13* elucidates the situation. Here, the distillate yield is plotted against temperature for distillation to three different softening point temperatures, while the corresponding pressures are represented by 'dashed' straight lines. In each distillation the distillate yield increased until a

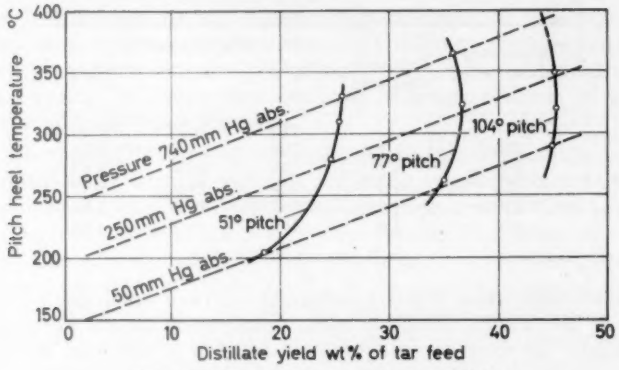

Figure 13. Further flash vaporization yields

temperature of about 320°C was reached. Apparently, strong thermal forces are necessary to effect the dissociation of complexes needed to get the maximum distillate yield.

Efforts have been made to determine by careful analysis of the distillate fractions obtained under the different distillation conditions whether it is a certain group of constituents which is most firmly associated. From work to date it appears that association is not limited to a certain group of compounds.

If high temperatures are required to overcome the strong association forces of complexes present in pitches, then two pitches of equal softening point, one having been produced at the low temperatures of vacuum distillation, and the other at the temperatures corresponding to atmospheric pressure distillation, should have different structures. This was actually demonstrated by the following experiments.

Two samples of pitches of 51°C softening points (R & B), one made by flash distillation at 50 mm of mercury pressure and 210°C, and the second by flash distillation at 700 mm of mercury pressure and 335°C, were each remelted under total reflux at 150°C and their softening points re-checked. They were 51·4 and 51·2 respectively. The two samples were then heated in an autoclave under total reflux to 324°C and next cooled to 150°C. The softening points of the samples were then again determined with the result that the first had decreased to 42°C, while the second had increased to 53°C. In neither case was there evolution of gases.

Finally, the existence of association forces of varying intensities, even in coal tar itself, was established by the following test series. Dehydrated coke-oven tar was pumped through a heated coil under sufficient pressure to avoid

vaporization. The heated tar was then cooled to below 100°C and was withdrawn from the pressurized zone. The viscosity of the thus-treated tar was lower than that of the original dehydrated tar. The magnitude of the viscosity reduction was directly dependent upon the temperature to which the tar had been heated and upon the exposure time. *Table 5* illustrates some of the experiments.

Table 5

Maximum treating temp. °C	*Exposure time, min*	*Viscosity, cS at:* 59°C	98·5°C	150°C
Original tar	—	358	29·3	6·06
250	1·1	298	25·6	5·74
275	1·1	288	24·9	5·62
325	1·1	232	21·9	5·17
350	1·1	193	20·6	5·04
374	1·0	179	19·9	4·88

The tar sample which had been heated to 325° and which had a viscosity at 98·5°C of 21·9 cS was stored at room temperature for six weeks and then tested again. Its viscosity had increased to 22·5. It was next stored for 18 hours at 100°C. Its final viscosity was 23·1 cS. This means that the association and dissociation processes are not reversible. Perhaps there is needed for the strong complex formation the shock-cooling process to which the tar vapours are exposed when they flow from the hot silica surfaces of the coke oven to the cool collecting main within less than a second.

CONCLUSION

Coal tar, and coal-tar pitch even more so, are colloidal systems containing clusters of aromatic condensed-ring compounds as the dispersed phase. The x-ray diffraction data present the strongest evidence in support of this conclusion with the temperature-dependence of the energy of activation of viscous flow furnishing corroborating information.

From a study of the viscosity properties of a non-filtered tar and the corresponding filtered tar, it is deduced that the tar-insoluble phase, C-1, is not 'inert' material but interacts with the matrix of the tar. There is evidence that, on heating, some of the tar-insoluble phase goes into solution leaving behind somewhat smaller particles of higher density. This interaction is not surprising because x-ray diffraction data indicate that the tar-insoluble phase is very similar to pitch itself. Judging from a statistical survey of possible molecular configurations having the atomic hydrogen-to-carbon ratio of the tar-insoluble phase, its molecular weight was estimated to be less than 2000.

As has been known for some time, the matrix of coal tar or coal-tar pitch is made up of a large number of aromatic condensed-ring compounds. Their molecular weights are well below 1000. With pitch, most of the molecules contain not more than seven and not less than three condensed rings. The high ratio of aromatic carbon atoms to total carbon atoms indicates little substitution by methyl groups.

The relatively low average molecular weight of the pitch matrix is surprising because, at room temperature, pitches appear to be solid substances. An explanation for this behaviour is the existence of strong association forces. At room temperature, they may amount to more than 20 kcal per mole. As the temperature increases, their magnitude decreases. But, even at 150°C, the association forces in coal tar still amount to more than 2 kcal per mole. Some dissociation phenomena are apparent even at higher temperatures as indicated by the results of flash-distillation experiments. In these experiments increasing oil yields were obtained when the distillation pressure and distillation temperature were increased until at about 330°C a maximum was reached. These increasing oil yields were obtained although residues of identical softening point were being produced.

When samples of these residues were exposed to a temperature of about 330°C, it was found that the softening point of a sample produced under the mild conditions of vacuum distillation had dropped some 10°C because at the high temperatures some of the molecular complexes dissociated into smaller units. This was not observed on the pitch sample produced by distillation under atmospheric pressure at about 330°C. A decrease in viscosity was also observed when dehydrated coke-oven tar was pumped through a heated coil under sufficient pressure to prevent vaporization. The magnitude of the viscosity decrease was a function of the maximum temperature of the heat treatment.

Some insight was obtained into the manner in which some of the association forces operate. X-Ray diffraction studies showed that coke oven tar has infrequent order with molecules being spaced some 5·5 Å apart. As the tar is distilled, the resulting pitches show increased order with a spacing of about 4·5 Å. Finally, as expected, pitch coke has more order than any of the other samples studied, with a spacing of 4·24 Å. The ordered regions, although not crystalline, can perhaps best be interpreted by 'clusters' such as postulated for the 'turbostratic structure' of the vitrinites in coal. The clusters consist of stacks of flat condensed-ring molecules.

Finally, viscosity measurements show that coke oven tar and pitch behave like simple liquids following the laws of Newtonian flow. Experimental results as well as viscosity concepts suggested by Glasstone *et al.*, revealed that coke oven tar and pitch are highly associated. An analysis of the change of viscosity with temperature showed that the energy of activation for flow changes linearly with temperature.

The author expresses his gratitude to Dr H. Raich for his painstaking work on the viscosity properties of coal tar, to Dr S. Ohlberg for the X-ray examinations of tar and pitch samples, to Mr John S. Lagarias for his counsel on many of the physical concepts, and to Koppers Co., Inc. for permission to publish this paper.

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Further Studies on the Mechanism of the Oxidation of Coal

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The earlier work on the mechanism of oxidation of coal has been extended especially to the consideration of the stability of the aromatic nucleus in coal under low temperature conditions in air. Further examination of the ring indices, $2(R-1)/C$ for a number of coals and vitrains, oxidized in air at 170°C, indicates a substantial increase of ring index on oxidation thus confirming the earlier findings. The stability of the ring system in coal during low temperature oxidation also appears to be supported by oxidation studies of some polynuclear substances (3- and 4-ring system) and of semicoke or char. Two stages in coal oxidation have been indicated: one below 220°C during which the coal structure is reduced to its aromatic skeleton, and the other, above 220°C wherein rupture of rings sets in. Attention has been drawn to the constancy of the H/C *and* C/(O + C) *atomic ratios of 'fully' oxidized residues of vitrains in the bituminous range* irrespective of rank, *indicating, possibly, a similar pattern and size of the ultimate structural units of coal, at least for coals of carbon contents between 80 and 86 per cent.*

OXIDATION is one of the recognized techniques used in the elucidation of an organic structure and as such it has been frequently employed in the study of coal constitution. Of the different oxidizing agents, air and oxygen are preferred as they enable a progressive study to be made of the physical and chemical changes brought about in the complex structure of coal at different stages of oxidation particularly under mild conditions. [Such controlled oxidation can only be helpful in probing into different parts of coal structure.] The work of R. V. WHEELER and his collaborators[1,2] has thrown much light on the general effects of the oxidation on coal and its petrological components, particularly in relation to the physical and chemical changes. More significant, however, to the study of coal constitution has been the work of F. FISCHER and H. SCHRÄDER[3], W. A. BONE and R. QUARENDON[4] and that of L. HORTON[5] recently, as these have led to the recognition of the essential aromatic (benzenoid) character of coal. Further advances in the subject will require knowledge of the mechanism of the oxidation of coal and in this connection the recent work of B. K. MAZUMDAR and others[6] and of D. W. VAN KREVELEN[7] might be considered to have made a significant contribution.

The mechanism of the oxidation of coal in air at 170°C advanced by B. K. MAZUMDAR and his collaborators[6] on the basis of a study of ring indices indicates that the aromatic ring system of coal remains unaffected even over a prolonged period of oxidation and that the large amount of functional oxygen groups (mainly carboxyl) which is produced, results from the oxidation of aliphatic and alicyclic structures around the aromatic nucleus of coal. This postulate of selective oxidation under low temperature conditions is not in accord with the views of H. H. STORCH[8] and of F. J. HUNTJENS and D. W. VAN KREVELEN[9]. The apparent decrease of ring index on oxidation observed

by Storch was shown to be due to the omission of the corrections to the H/C atomic ratio of the oxidized coal which are necessary to allow for its functional oxygen groups. F. J. HUNTJENS and D. W. VAN KREVELEN[9] also found a slight lowering of ring indices on oxidation of coal, but as neither the temperature of oxidation is known nor whether in the calculation of the ring index due corrections to H/C were made, no detailed study of the work is possible in relation to the mechanism of oxidation advanced in the present paper.

A revised calculation of ring index has since been made for two coals studied earlier[6]. In the earlier study the approximate form R/C was calculated. The more precise ring index $2(R-1)$/C could not be calculated but its evaluation has now been made possible by the recent publication of a graphical densimetric method[10] (H/C versus M_C/d). Accordingly, the ring index, for the two oxidized coals studied earlier has been recalculated and the results along with other relevant data are presented in *Table 1*.

Table 1. Ring indices of coals and of their oxidized residues

Sample	C %	H %	$\left(\frac{H}{C}\right)_{exp.}$	$\left(\frac{H}{C}\right)_{corr.}$	d	$\left(\frac{M_C}{d}\right)_{exp.}$	$\left(\frac{M_C}{d}\right)_{corr.}$	f_a	$\frac{2(R-1)}{C}$
Original coal	80·7	5·3	0·793	0·817	1·300	11·54	10·50*	0·76	0·42
Oxidized coal	67·8	2·1	0·372	0·576	1·607	11·16	8·47*	0·80	0·62
Oxidized coal	67·8	2·1	0·372	0·576	1·607	11·16	9·30†	0·90	0·52
Original coal	90·3	4·9	0·646	0·651	1·310	10·15	9·83*	0·89	0·46
Oxidized coal	76·0	2·4	0·379	0·518	1·570	10·06	8·36*	0·83	0·65
Oxidized coal	76·0	2·4	0·379	0·518	1·570	10·06	8·75†	0·90	0·58

* Correction according to van Krevelen and Chermin's formula[12]:

$$\left(\frac{M_C}{d}\right)_{corr.} = \left(\frac{M_C}{d}\right)_{exp.} - \left[8{\cdot}1\,\frac{O}{C} + 6{\cdot}4\,\frac{N}{C} + 12{\cdot}5\,\frac{S}{C}\right]$$

† Correction according to the revision of the above formula made by the writers; in view of the changed pattern of oxygen groups in the oxidized coal, it has been found that the overall correction factor for O/C in the formula should be nearly 6·0 instead of 8·1. The calculation of ring indices of oxidized coal is, however, shown above by using both of the correction factors. van Krevelen's correction factor for O/C, which is *suitable only for normal coals*, when used for oxidized coals leads to apparently absurd values for aromatic carbon content of oxidized coals.

The ring indices of oxidized coals thus calculated are found to increase substantially, provided due corrections to the ratios H/C (atomic) and M_C/d are made. [The nature of the corrections to H/C has already been published[6]; that for M_C/d is briefly indicated in a footnote to *Table 1*.]

The above ring index calculation although indicative of the stability of the ring system under mild oxidation conditions cannot be taken as unequivocal, because of the approximations and assumptions which are made in such a statistical approach. Extension of the work has therefore been made to include a larger number of coals and particularly vitrains, and special consideration has been given to the evaluation of ring stability under mild oxidizing conditions by methods other than ring index calculations. In this connection, the oxidation characteristics of polynuclear hydrocarbons are relevant. Further, the critical temperature of oxidation at which the rupture of the aromatic ring systems in coal appears to set in has also been investigated. These studies are presented here.

OXIDATION OF VITRAINS

The earlier procedures[6] for the oxidation of the samples (in air at 170°C) and the analysis of the oxidized products were followed with four vitrain samples having carbon contents ranging from 81 to 90 per cent. Samples of the oxidized residues of each of the vitrains were taken at different stages of oxidation and examined for their elementary composition and functional oxygen group distribution. The results together with those for three samples of coals (including a lignite and an anthracite) treated similarly are presented in *Tables 2* to *8*.

It will be seen that the ultimate effect of oxidation on vitrains (*Tables 2* to *5*) is similar to that on the coals studied earlier. However, there are certain special features about the detailed course of oxidation of vitrains which are briefly enumerated below:

(*i*) Vitrains require 800 to 1200 hours oxidation to attain complete immunity towards further oxidation in air at 170°C, whereas coals require only 300 to 400 hours to attain the same condition. This relatively high rate of oxidation of the overall coals may be due to the catalytic effect of their considerable content of mineral matter (16 to 22 per cent).

(*ii*) The maximum uptake of oxygen fixed in the oxidized residues is roughly the same for both coals and vitrains (*Tables 2* to *8*). The ratio of the carbon contents of the oxidized residues and the original vitrains is practically constant (0·785 ± 0·015) *irrespective of rank*. The same is true for coals but the ratio is a little higher (0·84).

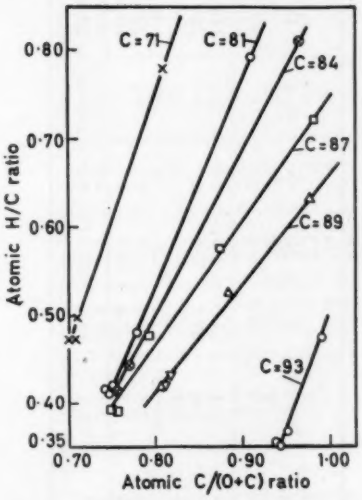

Figure 1. Changes of atomic H/C *and* C/(O + C) *ratios during 'full' oxidation of coal in air at 170°C.* ○ ⊗ □ △, *vitrains;* ×, *lignite;* ○, *anthracite*

(*iii*) The atomic ratio H/C of vitrains in the bituminous range (C = 80 to 90 per cent) progressively diminishes on oxidation but ultimately attains a constant value. Similarly, the C/(O + C) ratios converge to a definite value irrespective of the rank of the coal, at least for coals of carbon contents between 80 and 85 per cent (*Figure 1*). This suggests that coals in this range of carbon must be made up of similar structural units both in pattern and size.

Table 2. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation at 170°C in air: Vitrain 1. (C = *81·5 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash* %	C %	H %	N %	$S_{org.}$ %	O %	*Functional oxygen groups, per cent*				*Atomic ratio*	
								O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	3·1	81·5	5·4	1·8	0·4	11·0	0·9	5·0	1·8	3·2	0·91	0·79
208	+3·3	3·0	69·1	2·8	1·7	0·4	26·1	13·8	3·0	2·0	7·3	0·78	0·48
375	+0·9	3·2	—	—	—	—	—	14·0	3·2	2·5	—	—	—
600	*Nil*	3·3	67·1	2·6	—	—	—	14·3	—	—	—	—	—
830	−2·2	3·3	65·9	2·3	1·8	0·4	29·6	14·9	3·0	2·6	9·0	0·75	0·42
1000	−6·8	3·3	65·4	2·3	2·0	—	29·9	16·0	—	—	—	—	0·42
1250	−7·0	3·3	65·4	2·3	2·0	0·4	30·0	16·0	4·0	2·2	7·7	0·74	0·41
1300	−7·0	3·3	65·4	2·3	2·0	0·4	29·9	16·0	4·0	2·3	7·7	0·74	0·41

Table 3. Progressive changes in elementary composition and functional oxygen groups during oxidation at 170°C in air: Vitrain 2. (C = *84·4 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash* %	C %	H %	N %	$S_{org.}$ %	O %	*Functional oxygen groups, per cent*				*Atomic ratio*	
								O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	2·4	84·4	5·7	2·4	0·3	7·2	*Nil*	4·4	0·4	2·4	0·94	0·81
280	+2·5	2·4	—	—	—	—	—	12·3	4·2	0·4	—	—	—
400	−0·5	2·5	66·7	2·5	2·4	0·3	28·2	12·4	4·4	—	—	0·76	0·44
600	−4·2	2·5	65·7	2·3	—	—	—	14·0	2·1	2·0	—	—	—
830	−7·5	2·6	—	—	—	—	—	15·8	1·4	—	—	—	—
1000	−7·8	2·5	65·6	2 3	2·8	0·3	29·1	15·9	0·9	2·1	10·2	0·75	0·41
1200	−7·6	2·5	65·5	2·3	2·8	0·3	29·1	15·9	2·6	2·6	7·9	0·75	0·41

Table 4. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation in air at 170°C: Vitrain 3. (C = *87·3 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash %*	C %	H %	N %	$S_{org.}$ %	O %	*Functional oxygen groups, per cent*				*Atomic ratio*	
								O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	2·0	87·3	5·3	1·8	0·5	5·2	0·2	1·0	1·0	3·0	0·96	0·72
400	+8·6	1·9	70·7	2·8	1·7	0·5	24·4	8·3	2·0	—	—	0·79	0·47
620	+7·2	1·8	69·1	2·5	—	—	—	10·5	2·0	1·8	—	—	—
850	+4·0	1·9	67·7	2·3	—	—	—	14·0	—	2·0	—	—	—
1200	+0·9	2·0	67·5	2·2	1·7	0·5	28·1	14·0	2·0	2·3	9·8	0·76	0·39
1300	+0·8	2·0	67·6	2·2	1·6	0·5	28·1	14·0	2·2	2·2	9·7	0·76	0·39

Table 5. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation in air at 170°C: Vitrain 4. (C = *89·3 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash %*	C %	H %	N %	$S_{org.}$ %	O %	*Functional oxygen groups, per cent*				*Atomic ratio*	
								O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	1·6	89·3	4·7	2·1	0·6	3·3	*Nil*	0·8	0·6	1·9	0·97	0·63
100	+7·5	1·6	79·6	3·5	2·1	—	14·4	1·1	4·6	—	—	0·88	0·53
280	+9·3	1·5	75·7	2·9	1·9	—	—	5·7	3·3	—	—	—	—
380	+9·5	1·5	75·3	2·9	—	—	—	6·0	3·3	1·7	—	—	—
550	+9·5	1·5	73·0	2·7	1·4	0·6	21·9	7·1	0·9	—	—	0·82	0·44
766	+9·5	1·4	72·9	2·6	1·9	0·5	22·1	8·0	0·9	2·2	11·0	0·81	0·42
1200	+9·5	1·4	72·9	2·6	1·9	0·6	22·2	8·0	1·0	2·2	10·9	0·81	0·42

Table 6. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation in air at 170°C: Lignite. (C = *71·5 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash* %	C %	H %	N %	O* %	*Functional oxygen groups as* O, *per cent*				*Atomic ratio*	
							O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	10·0	71·5	4·7	0·8	23·0	6·3	8·7	2·4	5·7	0·81	0·78
144	−13·2	10·6	—	—	—	—	14·6	7·7	—	—	—	—
265	−27·1	11·2	62·6	2·6	1·0	33·8	16·5	8·1	3·2	6·0	0·71	0·50
330	−26·0	12·1	—	—	—	—	16·7	7·3	4·0	—	—	—
385	−26·6	12·2	61·5	2·4	1·0	35·1	17·5	—	—	—	0·70	0·47
600	−26·4	12·2	61·4	2·4	1·0	35·2	17·5	7·4	4·0	6·2	0·70	0·47

* Including organic sulphur which may be neglected as total sulphur in the sample is below 0·5 per cent.

Table 7. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation in air at 170°C: Overall coal. (C = *85·15 per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Loss or gain in weight*	*Dry ash* %	C %	H %	N %	O* %	*Functional oxygen groups as* O, *per cent*				*Atomic ratio*	
							O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	$\frac{C}{(O+C)}$	H/C
0	—	16·0	85·2	5·7	2·2	7·0	0·3	2·2	0·3	4·2	0·94	0·80
160	3·4	15·7	70·8	2·7	—	—	8·1	—	—	—	—	—
240	2·1	15·8	69·5	2·5	—	—	11·3	—	—	—	—	—
380	−5·0	16·3	67·9	2·4	2·4	27·4	13·8	8·1	0·6	4·9	0·77	0·42
592	−5·1	17·2	67·2	2·4	2·4	28·0	14·3	4·0	2·6	7·1	0·76	0·42
650	−5·0	17·2	67·2	2·4	2·4	28·0	14·3	4·0	2·8	6·9	0·76	0·42

* Includes organic sulphur which may be of the order of 0·3 per cent.

Table 8. Progressive changes in elementary composition and functional oxygen groups in coal during oxidation in air at 170°C: Anthracite. (C = 93·2 *per cent*) (*All data expressed on dry mineral matter free basis*)

Hours of oxidation	*% Gain in weight*	C %	H %	N %	(O + $S_{org.}$) (*by diff.*) %	*Functional oxygen groups as* O, *per cent*					*Atomic ratio*	
						O_{COOH}	O_{OH}	O_{CO}	$O_{unaccounted}$	O_{total}	$\frac{C}{(O+C)}$	H/C
0	—	93·2	3·5	1·5	1·8	*Nil*	*Nil*	*Nil*	1·8–0·5* =1·3	1·3	0·99	0·47
200	1·9	90·2	2·7	1·5	5·6	0·6	1·8	1·5	1·2	5·1	0·96	0·36
400	3·0	89·5	2 6	1·5	6·4	0·7	2·0	2·0	1·2	5·9	0·95	0·35
600	4·0	88·7	2·7	1·5	7·1	1·9	2·1	2·2	0·4	6·6	0·94	0·36
800	3·9	88·1	2·5	1·4	8·0	2·1	2·1	2·3	1·0	7·5	0·94	0·34
1000	4·0	88·1	2·6	1·4	7·9	2·1	2·1	2·4	0·8	7·4	0·94	0·35

* Assumed value for organic sulphur.

In contrast to bituminous coal, lignites and especially anthracites must have markedly different structures for their ultimate units as is indicated by the significantly different H/C and C/(O + C) ratios of their oxidized residues (*Figure 1*).

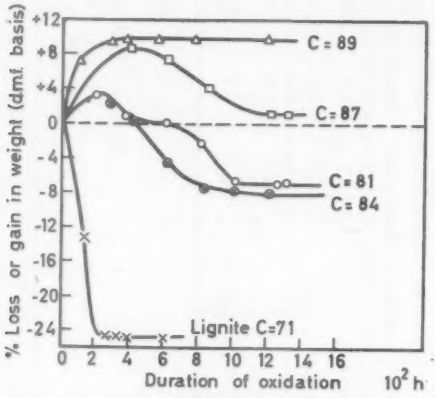

Figure 2. Percentage loss or gain in weight during oxidation of vitrains in air at 170°C

(*iv*) It will be seen (*Figure 2*) that all the vitrains irrespective of rank gain in weight within the first 200 hours of oxidation and afterwards with continued oxidation (except for the highest rank vitrain studied, C = 90 per cent) the gain is offset to varying degrees depending on the rank before complete immunity towards further oxidation is attained. Finally, the lower rank vitrains (C < 85 to 86 per cent) indicate an overall loss in weight on 'complete' oxidation (*Figure 2*), whereas higher rank vitrains (C > 86 per cent) gain in weight permanently; the higher the rank, the more is the gain. The same trend also is true for higher rank coals (C ~ 90 per cent). In contrast, however, the lower rank coals suffer a loss in weight from the beginning of oxidation (*Figure 3*), the lower the rank, the greater is the loss.

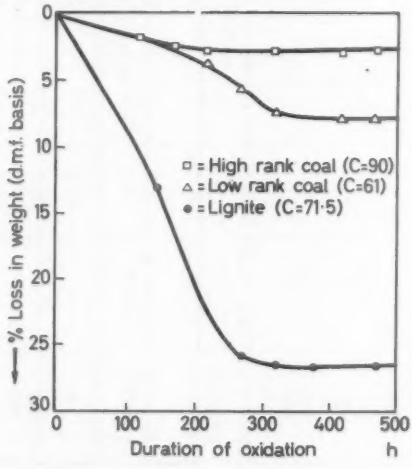

Figure. 3. Percentage loss in weight during oxidation of coals in air at 170°C [*Reproduced from* MAZUMDAR, B. K. *et al. Fuel, Lond.* 1958, **37**, 495]

(*v*) A qualitative difference is indicated in the manner of oxidation of coals and vitrains especially as regards the extent to which the oxygen taken up during the oxidation appears as functional groups. With the coals[6] it is found that at any stage of oxidation practically all the additional oxygen appears as reactive groups, the major form being carboxyl, and that the oxygen, not accounted for as functional groups, originally present in the coal (presumably as ether and/or heterocyclic oxygen) appears to remain intact throughout the course of oxidation. The trend of oxygen addition and its appearance in the form of functional groups is not, however, the same for vitrains: a large part of the additional oxygen (*Tables 2* to *5*) is non-functional and increases with the rank of the vitrains. The nature of this 'extra' non-functional oxygen, in the case of oxidized vitrain, has been investigated by reductive acetylation and has been found to be mainly quinonoid in nature. The results are shown in *Table 9*.

Table 9. Unaccounted oxygen in oxidized vitrain and reductive acetylation

Samples	*Functional oxygen before reduction*			$O_{accounted}$ *by reductive acetylation*	$O_{quinone}$	$O_{unaccounted}$ *(even after reductive acetylation)*
	O_{OH}	O_{CO}	$O_{unaccounted}$			
Vitrain C = 81·5%						
1. *Oxidized 830 h*	3·0	2·6	9·0	7·2	4·2	7·4
2. *Oxidized 1 250 h*	4·0	2·2	7·7	6·4	2·4	7·6
Vitrain C = 84·4%						
1. *Oxidized 160 h*	4·0	0·6	11·2	6·5	2·5	9·3
2. *Oxidized 1 000 h*	0·9	2·1	10·2	7·2	6·3	5·6
Vitrain C = 89·3%						
1. *Oxidized 250 h*	3·3	1·0	9·6	7·0	3·7	6·9
2. *Oxidized 700 h*	0·9	2·2	11·0	8·4	7·5	5·7

The initial gain in weight on oxidation of all vitrains irrespective of rank is probably due to the formation of considerable amounts of quinone groups which possibly precedes the oxidation of aliphatic and alicyclic carbon, which in turn results in the gain in weight being reduced in varying degrees (*Figure 2*).

(*vi*) Ring indices of oxidized vitrains have also been calculated. These substantiate the earlier findings[6] of the stability of the aromatic ring systems in coal. The results for two vitrain samples are shown in *Table 10*.

Table 10. Ring indices of two vitrains and their oxidized residues

Sample	C %	H %	$\left(\frac{H}{C}\right)_{exp.}$	$\left(\frac{H}{C}\right)_{corr.}$	d	$\left(\frac{M_C}{d}\right)_{exp.}$	$\left(\frac{M_C}{d}\right)_{corr.}$	f_a	$\frac{2(R-1)}{C}$
Original (V3)	87·3	5·3	0·725	0·730	1·305	10·59*	10·06	0·85	0·42
Oxidized	67·6	2·2	0·387	0·567	1·600	11·11	8·41	0·80	0·63
Oxidized	67·6	2·2	0·387	0·567	1·600	11·11†	9·14	0·90	0·53
Original (V2)	84·4	5·7	0·813	0·816	1·260	11·30*	10·60	0·74	0·44
Oxidized	65·5	2·3	0·416	0·628	1·582	11·54	8·62	0·78	0·59
Oxidized	65·5	2·3	0·416	0·628	1·582	11·54†	9·30	0·84	0·53

* † See footnotes under *Table 1*.

OXIDATION OF POLYNUCLEAR COMPOUNDS

A study of the oxidation characteristics of polynuclear compounds having some probable resemblance to the unit structure of coal is relevant and has been attempted to provide additional evidence on the mechanism of oxidation of coal. To this end, a few polynuclear substances, such as alizarin, fluorescein, pyrene, chrysene, and 2,3-dimethylanthraquinone, were subjected to the same mode of oxidation as had been applied to coal (in air/oxygen at 170°C). None of these 3- and 4-polycondensed ring systems was found to undergo rupture of the rings during 500 to 1000 hours oxidation. The results of the oxidation of these substances are presented in *Table 11*.

The melting point and elementary analysis of alizarin and fluorescein did not change. Pyrene and chrysene samples were not obtained pure. They were found to sublime appreciably at 170°C and accordingly were oxidized in a sealed tube in an atmosphere of oxygen. Conditions were regulated so that the pressure of the oxygen did not rise above 2 to 3 atmospheres. After oxidation for 1000 hours under these conditions, the gas in the sealed tube in each case was examined for water, carbon monoxide and carbon dioxide. No trace of these gases was found, indicating, apparently, the stability of the four-ring systems in these compounds. Detailed study, however, of other changes, which might have occurred on the periphery of the structure without the production of gases (e.g. formation of quinone and/or hydroxyl groups) has not yet been made. 2,3-Dimethylanthraquinone which was obtained pure was also oxidized in a sealed tube, and the products examined in a similar way. No water, carbon monoxide or carbon dioxide could be detected in the gas. The melting point of the substance remained unchanged, indicating not only the stability of the ring system but also of the methyl groups attached to it. The immunity towards oxidation of the methyl groups in this structure under these experimental conditions is significant and indicates that such groups may have a high degree of stability conferred upon them by a suitable constitutional environment.

The complete stability of the different polynuclear ring systems under the stated conditions of oxidation is considered to lend support to the suggested mechanism of oxidation of coal.

OXIDATION OF SEMICOKE AND CHAR

Work at the Cavendish laboratory[11] on the x-ray diffraction patterns of coal has indicated that the size of the carbon lamellae does not appear to increase significantly during carbonization up to and at 600°C; only the 'disordered' carbon is largely removed in the process. In view of this, it was thought that a study of the stability of the ring systems in semicoke or char might be of direct significance to coal.

Two samples of semicoke obtained from two coals (C = 87 and 90 per cent) were oxidized in a similar manner over a prolonged period. The results of the oxidation are presented in *Table 12*.

Although oxidation was continued for more than 1000 hours, practically no carboxyl groups were formed, nor was there any tangible loss of carbon from the system. Peripheral oxidation is indicated by the gain in weight

Table 11. Oxidation of known polynuclear substances in air/oxygen at 170°C

Substance	Physical and chemical data of pure substances			Oxidation condition	Hours of oxidation	Analysis of gaseous oxidation products			Melting point, °C		Elementary analysis			
											Before		After	
	Molecular formula	Molecular weight	Melting point °C			H_2O	CO_2	CO	Before	After	C %	H %	C %	H %
Alizarin	$C_{14}H_8O_4$	240	290	*In air at 170°C*	500	—	—	—	293	293	69·8	3·3	69·7	3·3
Fluorescein	$C_{20}H_{12}O_5$	332	314 *to* 316	*Same as above*	430	—	—	—	320	320	71·8	3·5	72·0	3·6
Pyrene	$C_{16}H_{10}$	202	149 *to* 150	*In closed tube filled with oxygen at 1 atm and 170°C*	500	*Nil*	*Nil*	*Nil*	*No sharp melting point*		—	—	—	—
Chrysene	$C_{18}H_{12}$	228	254	*Same as above*	500	*Nil*	*Nil*	*Nil*	*No sharp melting point*		—	—	—	—
2,3-Dimethyl-anthraquinone	$C_{16}H_{12}O_2$	236	210	*Same as above*	1000	*Nil*	*Nil*	*Nil*	208	208	81·4	5·1	81·3	5·0

Table 12. Oxidation of semicoke (prepared at 600°C)

Sample	Dry wt g	Analysis (dry basis)				Hours of oxidation	Wt of oxidized sample, g (dry)	Analysis of oxy-coke (dry basis)				Input		Output		O_{COOH} of oxy-coke
		Ash %	C %	H %	N + S + O %			Ash %	C %	H %	N + S + O %	C g	H g	C g	H g	
1. *600°C: coke from vitrain (C = 87%)*	4·864	2·6	88·9	2·8	5·7	1000	5·532	2·3	76·9	2·7	18·1	4·28	0·014	4·25	0·015	*Nil*
2. *600°C: coke from coal (C = 90%)*	4·980	27·2	66·1	2·0	4·8	980	5·265	25·2	61·6	2·3	9·9	3·29	0·097	3·24	0·122	*Nil*

which may possibly have been due to the formation of quinone and/or hydroxyl groups. The stability of the ring system of semicoke or char and the fact that its ring size is nearly the same as in the coal obviously supports the mechanism of oxidation of coal presented here. The large amount of carboxyl groups formed on oxidation of coal must, therefore, be attributed to the oxidation of aliphatic and alicyclic structures around the periphery of the aromatic nucleus.

CRITICAL TEMPERATURE FOR THE OXIDATION OF AROMATIC RING SYSTEMS IN COAL

The question naturally arises as to the temperature of oxidation at which the rupture of the ring system in coal commences. This question has been investigated by a continuous oxidation of coal at different temperatures, in an apparatus designed to permit determination of any gaseous products of oxidation, e.g. carbon monoxide, carbon dioxide, etc. Each sample of coal was oxidized at temperatures of 170° to 300°C in 10° steps, the oxidation being continued at each temperature until no further evolution of carbon monoxide and carbon dioxide occurred. Material balances were determined as well as the content of carboxyl groups in the 'completely' oxidized samples obtained at each temperature of oxidation. The results for a coal sample and a vitrain are given in *Figures 4* and *5*.

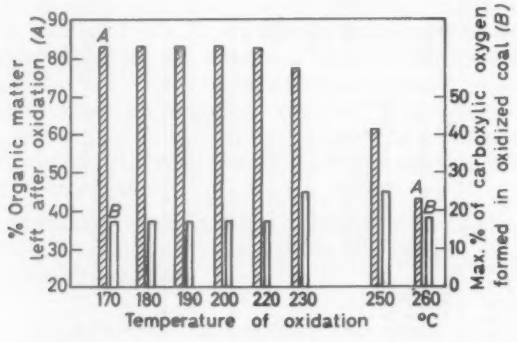

Figure 4. Maximum loss in weight and formation of carboxyl groups during oxidation of a coal (C = 80) at different temperatures in oxygen

For the coal sample, it will be seen that once the coal is 'completely' oxidized at 170°C, little further oxidation occurs until about 220°C or so, as is indicated by the constancy of the material balances and content of carboxyl groups (*Figure 4.*). The same is more or less true for the vitrain sample also (*Figure 5*). At about 230°C or immediately after, active oxidation starts once again, resulting in substantial losses of organic matter at a rapid rate. The carboxyl contents rise to 25 to 35 per cent (as oxygen) from the stabilized value of 15 to 18 per cent at 170° to 220°C. It would thus appear that there are two stages in coal oxidation, one below 230°C and the other above 230°C.

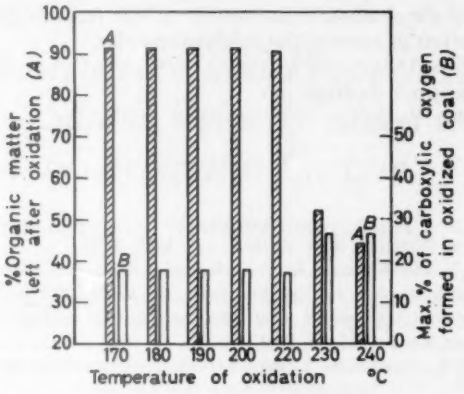

Figure 5. Maximum loss in weight and formation of carboxyl groups during oxidation of a vitrain (C = 81) *at different temperatures in oxygen*

The oxidation above 230°C, it will be seen (*Figures 4* and *5*), leads to complete combustion of the samples.

A critical study of the above results of oxidation at different temperatures and particularly of the immunity of coal towards further oxidation between 170° to 220°C and the sudden onset of oxidation once again at or after 230°C with the simultaneous creation of substantial contents of carboxyl groups indicates the initiation at this latter temperature of the rupture of the aromatic rings of the coal structure.

CONCLUSIONS

The following conclusions may be drawn.

(*1*) Coal can be selectively oxidized under low temperature conditions in air below 200° to 220°C, leaving its aromatic skeleton intact. This conclusion emerges from the study of the ring index of the oxidized coals or vitrains, and is further justified by the oxidation behaviour of certain polynuclear substances as well as of semicoke and char.

(*2*) Formation of large amounts of functional groups, chiefly carboxyl, results from the oxidation of alicyclic and aliphatic structures.

(*3*) Oxidation of the aromatic ring system of coal resulting in the rupture of rings sets in only after 220°C.

(*4*) The constancy of the H/C and C/(O + C) atomic ratios of the oxidized residues of vitrains *irrespective* of rank in the bituminous range indicates that coals with carbon contents of 80 to 86 per cent are composed of units whose structure, size and type are similar.

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Chemical Structure and Properties of Coal XXIV—Sound Velocity and Fraction of Aromatic Carbon

D. W. VAN KREVELEN, H. A. G. CHERMIN and J. SCHUYER

A method has been developed for calculating the fraction of aromatic carbon in coal from the velocity of sound, the density and the elementary analysis. This method is independent of the state of aggregation of the substance to be examined. Comparison has shown that the fraction of aromatic carbon as calculated from the molar sound velocity is practically equal to that found from the densimetric method.

ONE of the principal parameters in the statistical constitution analysis of coal (D. W. VAN KREVELEN and co-workers[1–3]) is the fraction of aromatic carbon. This quantity not only permits calculation of a second important parameter—the ring condensation index $\{2(R-1)/C\}$—but also contributes considerably to the derivation of a third parameter—the number of aromatic carbon atoms per structural unit. It is obvious therefore to search for ways of determining this quantity with the greatest possible accuracy. Up till now the fraction of aromatic carbon has been calculated from the density and the elementary analysis. In principle it might also be derived from the heat of combustion[4, 5]. The latter method, however, has the drawback that the fraction of aromatic carbon is calculated as a small difference between two large quantities, viz. the measured heat of combustion and the sum of the atomic increments; in consequence, the accuracy of the method leaves much to be desired.

The importance of the aromatic carbon fraction induced us to search for a procedure by which the results of the densimetric method could be checked. This new method would have to be independent of the state of aggregation of the substance to be examined, so as to be free from drawbacks analogous to those to which I. G. C. DRYDEN and M. GRIFFITH[5–7] have drawn attention with regard to the densimetric method.

Such a method has been found by making use of the additive character of the molar sound velocity.

MOLAR SOUND VELOCITY

List of symbols

a, b = constants
M = molecular weight
u = velocity
u_l = longitudinal sound velocity
D = density
$\mathfrak{E}$ = potential energy
R = number of rings

r = distance between two molecules
U = molar sound velocity
σ = Poisson modulus
U_{A-B} and U_A = contribution to the molar sound velocity by bond A—B and atom A
C, H, O etc. = number of carbon, hydrogen, oxygen etc. atoms
f_a = fraction of aromatic carbon
F = number of double bonds
C_a = number of aromatic C atoms.

RAMA RAO[8] demonstrated empirically that the molar sound velocity

$$U_M = u^{\frac{1}{3}} M/D \qquad \ldots\ [1]$$

for organic liquids is, within reasonable limits, independent of temperature. According to J. SCHUYER[9] the correctness of this finding can be proved theoretically if it is assumed that the interaction between the molecules in the liquid is governed by a potential of the shape

$$\varepsilon = -a/r^n + b/r^m \qquad \ldots\ [2]$$

Furthermore it has been shown empirically that the molar sound velocity can be calculated by addition of atomic and/or bond increments[10, 11]. A comprehensive survey of these bond increments is presented in *Table 1*, which has been compiled from data published by R. T. LAGEMANN and W. S. DUNBAR[12] and by A. WEISSLER[13].

Table 1

Bond A—B	*Increment* U_{A-B}	*Bond* A—B	*Increment* U_{A-B}
C—H	95·2	C—C	4·25
C—Cl	230	C=C	129
C—Br	247	C=S	319
C—I	305	C=O	186
$C—O_{alcohols}$	34·5	C=N	145
$C—O_{ethers}$	44·5	C≡N	285
C—S	99·5	O—H	99
C—N	20·7	N—H	90·7

It was found that no difference exists in the increment of the C=C double bond, in aromatic and olefinic compounds.

As we wish to use the additive character of the molar sound velocity for determining the structure of coal, it is advantageous to convert the bond increments into atomic increments and structural effects. These are given in *Table 2*.

Here again no difference has been made between aromatic and olefinic double bonds.

J. SCHUYER[9] also demonstrated that the calculated molar sound velocities of isotropic solids and liquids are comparable only if the longitudinal sound velocity u_l in the Rao function 1 is replaced by a corrected sound velocity

$$u_{l_{corr.}} = u_l\{(1 + \sigma)/3(1 - \sigma)\}^{\frac{1}{2}} \quad \ldots . [3]$$

where σ is the Poisson modulus.

*Table 2**

Atomic increment of structural effect	*Contribution* U_A	*Atomic increment*	*Contribution* U_A
C	8·5	O_{ether}	84·7
H	93·1	O=	181·7
F	120·5	$S_{thio-ether}$	194·7
Cl	227·9	S=	314·7
Br	224·9	—N<	13·8
I	302·9	—N=	159·3
$O_{alcohol}$	38·3	N≡	278·6

*The way in which the atomic increments can be calculated can best be shown by an example.

Given the two hydrocarbons C_nH_{2n+2} and $C_{2n}H_{4n+2}$; the molar sound velocity is now defined by:

Bond increments — Atomic increments

$$2U_{C_nH_{2n+2}} = \overbrace{2(n-1)U_{C-C} + 2(2n+2)U_{C-H}} = \overbrace{2nU_C + 2(2n+2)U_H}$$

$$U_{C_{2n}H_{4n+2}} = (2n-1)U_{C-C} + (4n+2)U_{C-H} = 2nU_C + (4n+2)U_H$$

By subtraction

$$-U_{C-C} + 2U_{C-H} = 2U_H$$

hence

$$\therefore U_H = U_{C-H} - \tfrac{1}{2}U_{C-C} = 95{\cdot}2 - \tfrac{1}{2}(4{\cdot}25) = 93{\cdot}1$$

The other values for the atomic increments were calculated analogously.

The Rao function 1 then changes into the Rao–Schuyer function

$$U_M = \{(u_l)^3 M/D\}\{(1 + \sigma)/3(1 - \sigma)\}^{\frac{1}{2}} \quad \ldots . [4]$$

For liquids ($\sigma = \frac{1}{2}$) this rather general relationship changes back into the Rao function. Hence, calculation of the molar sound velocity for an isotropic substance by means of the increments of *Tables 1* or *2* yields the value found from equation 4.

APPLICATION TO COAL

From the foregoing it appears that the molar sound velocity of a liquid or isotropic solid is given by

$$U_M = CU_C + HU_H + \Sigma OU_O + \Sigma NU_N + \Sigma SU_S + \ldots \text{structural increment} \quad \ldots . [5]$$

where the Σ symbols relate to the various forms of oxygen, nitrogen, sulphur etc. present in the molecule. We assume again (see Part V of this series[14])

that coal contains no triple bonds. The structural increment is therefore confined to the aromatic double bonds, the number of which is F, and the increment is U_F.

Since

$$F = \tfrac{1}{2} C_a \qquad \ldots. [6]$$

we get

$$U = CU_C + HU_H + \Sigma OU_O + \Sigma NU_N + \Sigma SU_S + \tfrac{1}{2} C_a U_F \qquad \ldots. [7]$$

The molecular weight of coal being unknown, the molar sound velocity is calculated per gramme atom of carbon; this gives

$$\frac{U_M}{C} = U_C + \frac{H}{C} U_H + \Sigma \frac{O}{C} U_O + \Sigma \frac{N}{C} U_N + \Sigma \frac{S}{C} U_S + \tfrac{1}{2} f_a U_F \qquad \ldots. [8]$$

where $f_a = C_a/C$.

To enable this formula to be applied to coal, the functional distributions of oxygen, nitrogen and sulphur must be known. According to L. BLOM, L. EDELHAUSEN and D. W. VAN KREVELEN[15], coal is composed predominantly of —OH, —O— and C=O groups. Starting from the data published by these authors we calculated the $O_{—OH}/C$, $O_{—O—}/C$ and $O_{C=O}/C$ ratios (see *Table 3*). For the oxygen contributions to these forms we chose (see *Table 2*): $U_{O_{—OH}} = 38{\cdot}3$, $U_{O_{—O—}} = 84{\cdot}7$ and $U_{O_{C=O}} = 181{\cdot}7$. Less is known about the functional distribution of nitrogen. According to W. FRANCIS and R. V. WHEELER[16] and C. W. SHACKLOCK and T. J. DRAKELEY[17], by far the larger portion of nitrogen is present in cyclic configurations. For nitrogen therefore we chose only one contribution, viz. $U_{—N=} = 159{\cdot}3$. As the coals examined contained virtually no sulphur, the effect of sulphur has been disregarded. In consequence, we may write

$$\frac{U_M}{C} = 8{\cdot}5 + 93{\cdot}1 \frac{H}{C} + 38{\cdot}3 \frac{O_{—OH}}{C} + 84{\cdot}7 \frac{O_{—O—}}{C} + 181{\cdot}7 \frac{O_{C=O}}{C} + 159{\cdot}3 \frac{N_{—N=}}{C} + 60{\cdot}2 f_a \qquad \ldots. [9]$$

Formula 9 is the working equation for calculating the fraction of aromatic carbon in coal. To enable it to be applied, however, the reduced molar sound velocity must be known. This is calculated from the sound velocity by means

Table 3

% C	$\frac{H}{C}$ *	$\frac{O_{—OH}}{C}$ †	$\frac{O_{—O—}}{C}$ †	$\frac{O_{C=O}}{C}$ †	$\frac{N}{C}$ *	$\frac{M_C}{D^{20}}$ *	u_l m/s ‡	$\frac{U_M}{C}$ §	$60{\cdot}2\, f_a$ ‖	f_a
81·5	0·753	0·066	0·037	0·005	0·017	11·16	2318	138·9	51·0	0·85
85·0	0·757	0·048	0·018	0·005	0·016	11·02	*about* 2320	137·0	51·2	0·85
89·0	0·683	0·019	0·012	0·003	0·018	10·41	2336	129·9	52·7	0·87
91·2	0·594	0·004	0·016	0·001	0·015	9·84	2342	122·9	55·0	0·91
92·5	0·509	0·002	0·014	0·000	0·015	9·28	2391	116·7	57·2	0·95
93·4	0·440	0·001	0·012	0·000	0·015	8·86	2481	112·8	59·9	0·99

* According to ref. 15.
† Calculated from data from ref. 17.
‡ According to ref. 19.
§ Calculated from formula 4 after replacing M by M_C.
‖ Calculated from formula 9.

of equation 4. The data needed were taken from a paper by J. SCHUYER, H. DIJKSTRA and D. W. VAN KREVELEN[18]. From this article it appears that coal with more than 93·4 per cent carbon is elastically anisotropic. As formula 4 holds only for isotropic solids, this is the upper limit to the validity of the method. A dubious point in the latter publication is the maximum in the sound velocity versus carbon percentage curve at 85 per cent carbon. New measurements on a vitrain with 85 per cent failed to reproduce this value, and yielded a sound velocity of about 2320 m/s.

For the Poisson modulus we chose a value[19] of 0·345. All other data needed for the calculations were taken from a paper by van Krevelen and Chermin[14]. The fractions of aromatic carbon calculated by means of the new method, and the data used, have been compiled in *Table 3*.

DISCUSSION

Table 3 shows that the contributions from the fraction of aromatic carbon (column 10) are greater than one third of the 'measured' molar sound velocity per gramme atom of carbon. This means that, unlike in most methods of determining the structure from physical constants, the structural effect is no longer calculated as a difference between two large quantities. It may be expected therefore that the fraction of aromatic carbon determined from the molar sound velocity will be fairly accurate.

Table 4

% C	f_a (*Density*)	f_a (*Sound velocity*)	% C	f_a (*Density*)	f_a (*Sound velocity*)
81·5	0·83	0·85	91·2	0·93	0·91
85·0	0·84	0·85	92·5	0·95	0·95
89·0	0·89	0·87	93·4	0·97	0·99

Comparison of the results with the values found from the densimetric method (see *Table 4*) shows that the two values agree with each other within the accuracy limits of the densimetric method (three units in the second decimal). This agreement supports the correctness of the densimetric method.

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Quantitative Determination of Some Polyhydric Phenols

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A method is described for the quantitative analysis of polyhydric phenols involving paper chromatography and ultra-violet absorption measurements. Although calibration graphs are required the accuracy obtained is considered greater than that by using other available methods.

ALTHOUGH many methods for the analysis of monohydric phenols by gas chromatography, column chromatography and paper chromatography[1] have been described in the literature, much less information has been recorded on the analysis of polyhydric phenols. By using column chromatography W. BIELENBERG and co-workers[2,3] obtained qualitative data on some polyhydric phenols by means of azo dye formation. J. REIO[4] gives a very detailed description of a paper chromatographic method for the qualitative determination of phenol derivatives. The R_F values of six different solvent systems together with the corresponding colour reactions produced by ten standard reagents are given.

By modifying the paper chromatographic method of H. G. BRAY *et al.*[5], W. H. BLACKBURN and co-workers[6] have qualitatively separated a complex mixture of mono-, di-, and tri-hydric phenols in gas works ammoniacal liquor. More recently L. BARKER and N. W. HOLLINGWORTH[7] have evolved a column partition technique for the qualitative separation of many of the mono-hydric and several di-hydric phenols in ammoniacal liquor and have evaluated them quantitatively by means of ultra-violet measurements.

A. E. BRADFIELD and A. E. FLOOD[8] have also detected phenols of biological origin by direct ultra-violet spectral examination of the paper chromatogram. R. W. KEITH, D. LE TOURNEAU and D. MAHLUM[9] have used paper chromatography to separate phenols and have eluted the spots quantitatively by means of a solvent, followed by colorimetric determination of the amount of phenol in the solution.

The problem which we were investigating required a method which would separate completely and estimate accurately trace amounts of phenols in many types of gas works liquors and effluents. In particular, where these liquors have been successfully treated with bacteria under controlled conditions in order to reduce the phenol content by biological oxidation[10], it has been desirable to find which of these phenols were quickly and completely oxidized, and those which resisted bacterial oxidation. It was considered that no published literature gave an analytical method which was completely suitable for our particular problem, as column methods were suspect at really low concentrations. We have therefore made modifications to the

paper chromatographic method adopted by Blackburn and co-workers and have extended it to quantitative estimation by ultra-violet absorption measurements of the separated phenols, after their elution from the chromatogram by an organic solvent. Eighteen phenols may thus be determined with an accuracy of ± 2 per cent. With the exception of $\alpha + \beta$ naphthol, monohydric phenols have an R_F value of unity and thus do not interfere with the analysis.

APPARATUS

The chromatographic tank used for all our experiments was made entirely of glass and had the dimensions 2 ft $\times$ 2 ft $\times$ 1 ft. Chromatographic sheets were suspended from the head of the tank by being clamped between a pair of glass rods held together with rubber bands: these rods were supported on a ledge on both sides of the tank. The organic mobile phase was admitted to the trough by a glass tube inserted through the wall of the tank. An electromagnetic timing device allowed the solvent to flow into the trough from a reservoir at any preselected time. A Petri dish on the floor of the tank served to saturate the atmosphere before an experimental run commenced. The tank was sealed by means of an optically flat glass plate which rested over the open end and which was greased lightly to provide an air-tight seal.

A Beckman DK2 Ratio Recording Spectrophotometer was used for all measurements of optical density.

Accurate weighings of the pure phenols and the unknown mixtures to be chromatographically separated were carried out on an Oertling microbalance Model 141.

Calibration—The success of this method depends on very accurate calibration: each phenol used in preliminary experiments was therefore purified before being stored in a dark bottle. Methods of purification were fractional crystallization, zone melting and preparative paper chromatography. Whatman No. 3 chromatographic paper sheets were stored in large sealed polythene bags to prevent aerial contamination; this latter can cause the appearance of spurious peaks and 'tailing' of the true spots. Owing to our original uncertainty each phenol was chromatographed at several concentrations in the microgramme range and after elution from the paper in a solvent, its optical density was recorded at a particular wavelength maximum. The optical density was then compared with that obtained from an equal weight of the phenol which was dissolved directly in the solvent and the time of elution was adjusted to give the maximum complete extraction from the paper. Thus a graph was drawn for each phenol of concentration (as microgrammes in 5 ml of solvent) against optical density at the desired wavelength (*Figures 1*, *2* and *3*). This laborious procedure proved conclusively that Beer's law applies to all phenols tested over a comparatively wide range of concentration. No attempt was made to calculate the extinction coefficient at any absorption maxima, as it proved to be quite unnecessary in this approach. Literature values of absorption maxima vary considerably and they are usually to some extent dependent on the instrument used for obtaining them.

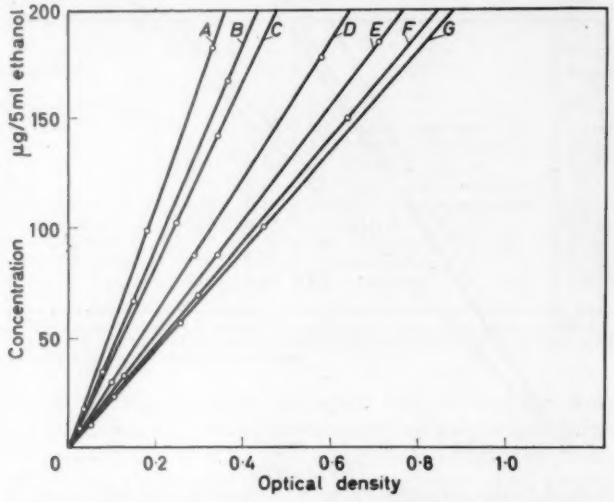

Figure 1. Calibration graphs of some dihydric phenols. A: 2-methyl resorcinol; B: 5-methyl resorcinol; C: 2,4-dimethyl resorcinol; D: 4,5-dimethyl resorcinol; E: 4-ethyl resorcinol; F: 4-methyl resorcinol; G: resorcinol

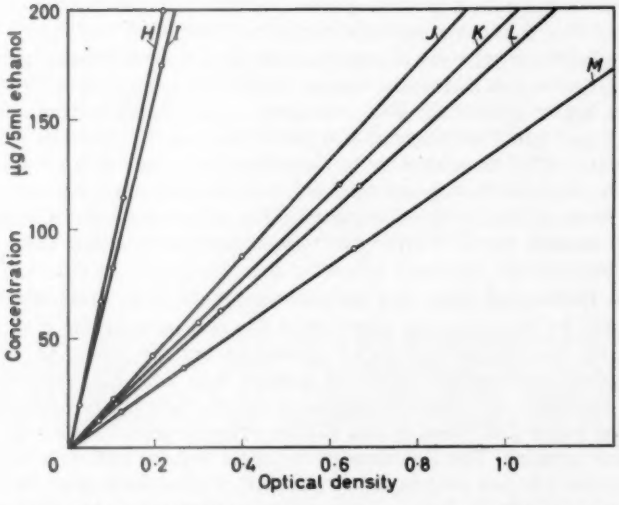

Figure 2. Further calibration graphs. H: pyrogallol; I: α-naphthol; J: 2,6-dimethyl quinol; K: β-naphthol; L: quinol; M: phloroglucinol

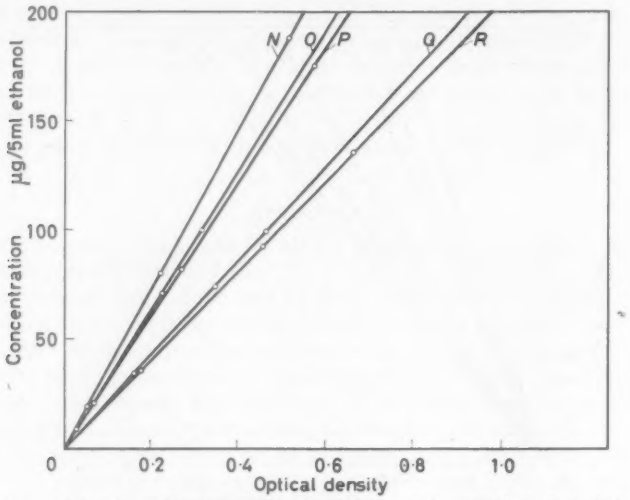

Figure 3. Further calibration graphs: N: 3,4-dimethyl catechol; O: 3-methyl catechol; P: 4,5-dimethyl catechol; Q: 4-methyl catechol; R: catechol

EXPERIMENTAL

The phenols to be analysed were either present as an aqueous syrup, having been concentrated by vacuum distillation at room temperature from dilute aqueous solution, or as a solid, in which case the latter was dissolved in a minimum amount of ethanol and this solution was used.

A known weighed concentration of the mixture was therefore spotted, by means of a capillary, on to a baseline which had been drawn across a sheet of Whatman No. 3 chromatographic paper of dimensions 137 cm × 117 cm. The weight of the spot usually varied between 100 and 600 microgrammes. This was to be run in parallel with a second unweighed spot of the same mixture, the weights of the two spots being approximately equal. After the spotted paper had been suspended in the tank for several hours to allow it to 'equilibrate' with the solvent vapour contained in a Petri dish on the floor of the tank, the solvent was run into the trough inside the tank and upward development of the paper commenced. The solvent used in all experiments was the organic phase of the mixture benzene: acetic acid: water = 3:3:1 (by volume).

When the solvent front had ascended approximately 50 cm the run was terminated by removing the paper from the tank and drying it in a gentle current of air. The strip of paper containing the run from the unweighed spot was cut out from the sheet and sprayed with a freshly prepared 0·1 per cent w/v solution of 2,6-dichloroquinone chloroimide in anhydrous ethanol. After the paper had dried it was further sprayed with 10 per cent sodium carbonate solution. The R_F values of the spots and the characteristic colours given by this alkaline reagent served as proof of identification of the component phenols (*Table 1*). 'Marker' phenols were also run in parallel so that if if the R_F values had altered due to a change in certain variables such as a

Table 1

Compound	*Wavelength (Å)*	R_F	*Compound*	*Wavelength (Å)*	R_F
1. *Phloroglucinol*	2674	0·02	10. *4-Ethyl resorcinol*	2800	0·40
2. *Pyrogallol*	2671	0·06	11. *2,6-Dimethyl quinol*	2888	0·42
3. *Quinol*	2931	0·10	12. *4-Methyl catechol*	2825	0·46
4. *Resorcinol*	2753	0·12	13. *4,5-Dimethyl catechol*	2857	0·52
5. *5-Methyl resorcinol*	2738	0·18	14. *2,4-Dimethyl resorcinol*	2778	0·57
6. *4-Methyl resorcinol*	2802	0·25	15. *3-Methyl catechol*	2746	0·60
7. *2-Methyl resorcinol*	2729	0·30	16. *3,4-Dimethyl catechol*	2785	0·72
8. *4,5-Dimethyl resorcinol*	2810	0·32	17. *β-Naphthol*	2730	0·97
9. *Catechol*	2778	0·36	18. *α-Naphthol*	2958	0·99

NOTE: 3,5-Dimethyl catechol is omitted from *Table 1* owing to an insufficiency of the pure compound needed for calibration. Both the 3,4- and 3,5-isomers have similar R_F values, but may be separated over a length of 50 cm if only relatively small concentrations of both are present.

sudden change in temperature or incomplete saturation of the tank atmosphere, then the relative positions of the phenols could still be easily determined. This strip of paper containing the visualized phenolic spots was placed back in position on the chromatographed Whatman sheet. The corresponding area for each phenol present in the run from the first weighed spot was cut out, carefully rolled into a tight roll with forceps and immersed for 24 hours in 5 ml of spectroscopic grade ethanol. The absorption spectrum of each solution was then recorded in the range 2500 to 3200 Å and the optical density measured for each phenol at a determined wavelength maximum. The optical density was never allowed to exceed 0·6. The phenol concentration in the solvent could therefore be read directly from the calibration graph. The solvent blank used in all these spectroscopic measurements consisted of ethanol in which had been immersed a similar area of blank chromatographed paper as that area containing the phenolic spot.

The importance of recording the spectrum over a fairly wide range of wavelength for each phenol cannot be overstressed. When dealing with unknown solutions the presence of other components which might chromatograph similarly to the compounds in question and which might also absorb ultra-violet light in the same region as these compounds is quite possible. Such compounds would normally be undetected if optical densities only were measured at wavelength maxima. Using a recording spectrophotometer the time taken for such a wavelength check would be only a few minutes, though to carry out such an operation with manually operated instruments would prove very tedious and hence precautions might become disregarded.

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A Note on the Relation of Specific Volume of Coals to their Hydrogen and Oxygen Contents

S. ERGUN, M. MENTSER and H. C. HOWARD

Analysis of density determinations on a number of coals and coal components by helium displacement has shown that the specific volume is a linear function of the hydrogen content on an atomic basis. Furthermore, the specific volume of natural graphite has been found to conform with this linear relationship. An error analysis of this linear relationship, using published and new data, showed a variance of only ± 1 per cent from the least-squares line and a correlation coefficient of 0·997. In examining molar volumes of organic compounds containing oxygen, it was observed that 'atom volume' of oxygen in ether linkages and ketenes was generally larger than that of carbon and the opposite was found to be true for oxygen in hydroxyl and quinone compounds. It is concluded that oxygen atoms in coals may have 'atom volumes' both smaller and larger than the average 'atom volume' of carbon.

THERE has been a great deal of interest in the density of coal. Its several petrographic components have been found to have different densities, a finding which has a practical consequence; coal components can be separated commercially by float-and-sink methods and utilized selectively. To the worker who is engaged in the study of coal constitution, an interesting feature of density is that it can be correlated with the hydrogen content.

R. E. FRANKLIN[1] measured helium densities of a series of coals having carbon contents ranging from 80 to 95 per cent by weight. She plotted specific volume against *weight* per cent hydrogen and observed a linear relationship from which she concluded that there is a fundamentally similar molecular structure in a wide range of different coals. Franklin's data are shown in *Figure 1*. Extrapolation of the straight line to the ordinate led to a specific volume of 0·54 cm^3/g, a value markedly different from the specific volume of graphite, 0·442 cm^3/g. She interpreted the difference as indicating that the 'fundamentally similar molecular structure' that exists in coals is markedly different from the structure of graphite. This interpretation was contrary to a widely held view that coals become graphite-like with metamorphism, a view that is supported by X-ray evidence.

The authors have measured the helium densities of Rhode Island meta-anthracite, a resin separated from a high volatile B bituminous coal and the isolated petrographic components of a high volatile A bituminous coal. It was found that the specific volumes lay on a straight line when plotted against *atom* per cent hydrogen; moreover, when extrapolated the line crossed the ordinate at 0·44, a value very close to the experimentally determined specific volume of graphite, 0·442 cm^3/g. This observation led the authors to replot Franklin's data against *atom* per cent hydrogen, as shown in *Figure 2*. The straight line in the figure is calculated by the method of least-squares using data of the authors (cf. *Table 1*).

An analysis of Franklin's data alone when correlated with *weight* per cent hydrogen, *Figure 1*, yielded a variance of $\pm$ 1·2 per cent from the least-squares line and an intercept of 0·53 $\pm$ 0·01. The specific volume of graphite differed from the intercept by 9σ (σ denotes root mean square error). A similar analysis of Franklin's data when correlated with *atom* per cent hydrogen, *Figure 2*, showed a variance of $\pm$ 0·9 per cent from the least-squares line

Table 1. Chemical composition and densities (by helium displacement) of coal components, meta-anthracite and graphite

Component	*Wt per cent ash*	*Ultimate analysis, wt per cent, M.A.F.*					*Helium density* g/cm³*
		H	C	N	O	S	
Ceylon graphite	2·9		99·8			0·2	2·264
Rhode Island meta-anthracite†	0·5	0·2	97·9	0·2	1·7		2·173
Fusinite from high volatile A bituminous coal (Hernshaw)	3·7	3·2	91·5	0·6	4·3	0·4	1·483
Micrinite from Hernshaw coal	7·9	4·8	85·9	0·7	8·0	0·6	1·322
Vitrinite from Hernshaw coal	1·4	5·3	85·8	1·6	6·6	0·7	1·291
Exinite from Hernshaw coal	3·1	6·5	86·2	1·1	5·5	0·7	1·215
Resin from high volatile B bituminous coal (Utah)	3·6	10·4	85·6	0·4	3·2	0·4	1·070

* Corrected for mineral matter content.
† Mineral matter removed with mixture of hydrochloric and hydrofluoric acids.

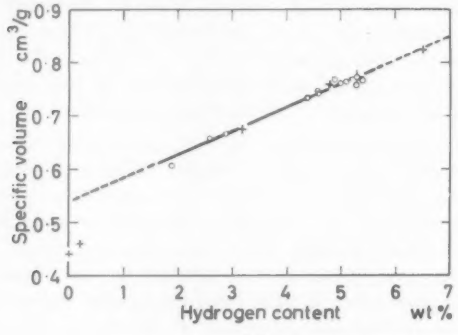

Figure 1. Relation between specific volume and weight per cent hydrogen: ○ data of Franklin, + data of the authors

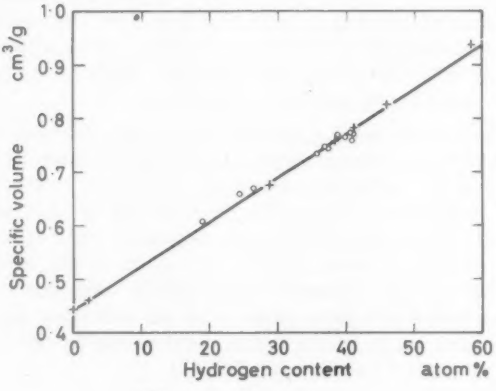

Figure 2. Relation between specific volume and atom per cent hydrogen: ○ data of Franklin, + data of the authors

(not shown) and an intercept of 0·48 ± 0·01, the specific volume of graphite differing by 3·5σ. Judging from the variance analysis, Franklin's data show equally good linear relationship with *atom* fraction of hydrogen and with *weight* fraction. The plot against *atom* fraction yields an intercept that is not significantly different from the specific volume of graphite. It should be noted here that Franklin's plot is consistent with the concept of additivity of 'atom volumes' (cf. J. TRAUBE[2]) of hydrogen and carbon, whereas the present plot is not.

Helium densities have also been reported by D. W. VAN KREVELEN and H. A. G. CHERMIN[3] for pure vitrinites selected to be representative of the coalification series, i.e. on vitrinites ranging from 70·5 to 96·0 weight per cent carbon. After correcting the density values for oxygen, nitrogen and sulphur content, these investigators found an empirical functional relationship between corrected density and the weight per cent of hydrogen, as shown in

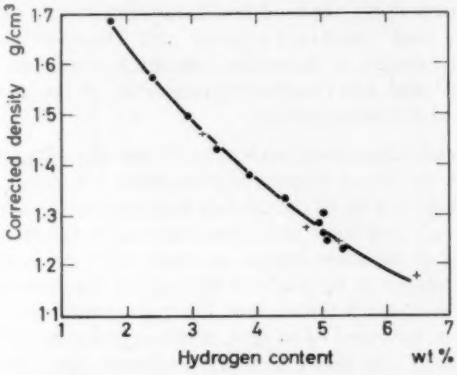

Figure 3. Relation between corrected density and weight per cent hydrogen: ● data of van Krevelen and Chermin, + data of the authors

Figure 3. Concentrates of petrographic components which van Krevelen and co-workers obtained from various coals also fitted the relationship of *Figure 3.* The linear relationship between specific volume of coal and hydrogen content on an atomic basis has been further studied by plotting van Krevelen and Chermin's data (using uncorrected density values) in *Figure 4.*

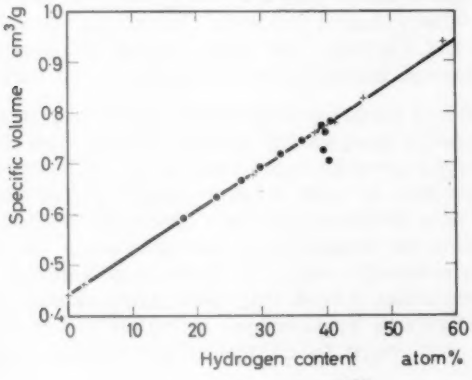

Figure 4. Relation between specific volume and atom per cent hydrogen: ● data of van Krevelen and Chermin, + data of the authors

Their data also fit the linear relationship and, when extrapolated, lead to the specific volume of graphite. In *Figure 4* the straight line again represents data of the authors.

An error analysis of the combined data, when correlated with *atom* hydrogen content, yielded a variance of $\pm$ 1 per cent from the least-squares line (which essentially agrees with that drawn using the authors' data) and a correlation coefficient of 0·997. The intercept was 0·444 $\pm$ 0·004 which coincides with the specific volume of graphite, 0·442 cm³/g. A similar analysis of the plot of the combined data against *weight* per cent hydrogen yielded a variance of $\pm$ 3 per cent, a correlation coefficient of 0·969 and an intercept of 0·53 $\pm$ 0·01. It is seen that specific volumes of coals show a very high degree of correlation with their *atom* hydrogen content and that specific volume at zero hydrogen content coincides with that of natural graphite.

Regarding the existence of a basically similar structure in a wide range of different coals, the modified linear relationship shown above suggests nothing more than Franklin's original plot. However, the trend of the present plot with decrease in hydrogen content is consistent with that shown by reflectance[4] and x-ray scattering intensities of coals[5], i.e. coals become graphite-like with metamorphism.

Coals containing more than 12 per cent oxygen by weight show deviation from the linear relation shown above (cf. *Figure 4* and ref. 3). Nevertheless the high degree of correlation between the specific volumes of a large number of coals and their hydrogen contents is interesting in view of the fact that some of the coals contain as much as 12 per cent oxygen. In considering the corrections to be made to density for the presence of oxygen, nitrogen and sulphur, van Krevelen and Chermin used 'atom volumes' given by Traube. 'Atom volumes' of oxygen in different forms (OH, C=O, C—O—C, etc.) as listed by the above authors are lower than the 'atom volume' of carbon. Thus oxygen would be expected to decrease the specific volume of coals. This may be true in general. However, while examining molar volumes of aromatic compounds, the authors have observed that the 'atom volume' of oxygen in ether linkages and in ketenes is very high. For example, the 'atom volume' of oxygen in diphenyl ether as calculated from the molar volumes (in solid state) of diphenyl and diphenyl ether is 28 cm³ which is far in excess of 5·5 cm³ for oxygen (in ether linkages) and 9 cm³ for carbon, the values adopted by van Krevelen and Chermin. The 'atom volume' of oxygen in hydroxyl and quinone compounds appears to be smaller than that of carbon.

From the above observation it would seem that oxygen-containing organic compounds need not necessarily have smaller specific volumes than those containing no oxygen, i.e. for a given hydrogen content. As an illustration, we have plotted specific volumes of some organic compounds containing oxygen against atom per cent hydrogen and have observed considerable scatter, both below and above the straight line representing coals. The plot is not shown here; it was essentially similar to *Figure 2* of Franklin[1]. It appears possible that oxygen atoms in coals may have 'atom volumes' both smaller and larger than the average 'atom volume' of carbon and, in coals containing less than 12 per cent oxygen, the average 'atom volume' of oxygen

may not be significantly different from that of carbon. The above-mentioned possibility may explain partially the high degree of correlation that exists between specific volume and hydrogen content.

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Some Observations on the Specific Surface of Coals

S. J. GREGG and M. I. POPE

The specific surface of a number of vitrains, representative of the whole coal range, have been determined by nitrogen sorption at 77°, 90° and 195°K and also by n-butane sorption at 273°K. The results lend general support to the views put forward by Zwietering and by Maggs, namely that activated diffusion of adsorbate molecules into the internal structure of coals occurs at low temperatures. Generally speaking, the specific surfaces calculated by n-butane adsorption agree satisfactorily with heat of wetting values obtained by other workers on a similar range of coals using methanol as wetting agent.

A GREAT deal of controversy still appears to exist as to the true interpretation of the measurements of the specific surface of coals, as determined by various methods.

The results obtained by sorption of argon or nitrogen at 77° or 90°K are known to be smaller, often by an order of magnitude, than those obtained by sorption, e.g. of butane[1, 2, 3] at or near room temperature, or by heat of wetting in methanol; the reported values determined by low temperature adsorption usually lie[1, 2, 6] below 15 $m^2 . g^{-1}$. Both F. A. P. MAGGS[7, 8] and P. ZWIETERING and others[2, 9] have drawn attention to the importance of temperature in such measurements and Maggs has found that the measured sorption of nitrogen and of argon on a number of coals *increases* with rise in temperature even though the sorption is only physical in nature and so would be expected to decrease. By way of explanation he has suggested that the coals contain fine constrictions of molecular size which serve as entrances to wider chambers; the passage through the constrictions is an activated process and so occurs far more rapidly as temperature rises. The adsorbate molecules are thus, at higher temperatures, able to reach, within the period of the experiment, parts of the internal surface which were excluded to them at lower temperatures.

Since specific surface is so important a parameter for coals, it was considered worth while to carry out a systematic investigation of a series of vitrains for which a body of other data has already been accumulated elsewhere. The sorption isotherms of nitrogen at 77° and 90°K, and of *n*-butane at 273°K, and one point on the isotherm of nitrogen at 195°K, have been determined and the specific surface area has then been calculated from the results.

EXPERIMENTAL

Some details of the vitrains are given in *Table 1*. The adsorption isotherms were determined gravimetrically using an auto-recording vacuum balance[10]; the samples were first outgassed to constant weight at 110°C, and the oven was then replaced by a constant temperature bath. Successive charges of

Table 1. Details of vitrains

No.	*Origin of vitrain*	*% Carbon (d.m.f.)*	*% Volatile matter*
1	*Blaenhirwaun, Pumpquart Seam*	94·0	5·0
2	*Coegnant, Gellideg Seam*	91·5	16·5
3	*Roddymoor, Ballarat Seam*	88·5	27
4	*Houghton Main, Parkgate Seam*	87·5	34
5	*Dinnington Main, Barnsley Seam*	85·0	37
6	*Markham Main, Barnsley Seam*	82·5	41
7	*Cannock Wood, Shallow Seam*	80·0	43
8	*Nailstone, Yard Seam*	78·5	43

gas were admitted to the sample and the pressure was read when the sample weight had become constant. The low temperature baths were liquid nitrogen (77°K), liquid oxygen (90°K), carbon dioxide–acetone (195°K) and ice–water (273°K). The *n*-butane was 99 per cent pure and the nitrogen was supplied as oxygen-free (white spot) from the British Oxygen Company.

RESULTS AND DISCUSSION

The specific surface area S was calculated from the sorption isotherms of nitrogen at 77° and 90°K and of *n*-butane at 273°K by the well known BET procedure[9], taking the cross sectional area of nitrogen as 16·2 Å² and of butane as 41 Å². At 195°K, however, the BET method is inapplicable since nitrogen is then above its critical temperature, so that sorption will not exceed a monolayer. A lower estimate of the area at this temperature can be obtained by assuming that at the maximum pressure attainable, 1 atm, the monolayer was complete, and again taking the cross sectional area as 16·2 Å². The actual specific surface area is likely to lie considerably above this but not by an order of magnitude.

Table 2. Apparent specific surface of selected vitrains as determined by adsorption

No.	*% C*	*Specific surface area, $m^2 . g^{-1}$*			
		N_2 *at 77°K*	N_2 *at 90°K*	N_2 *at 195°K*	n-C_4H_{10} *at 273°K*
1	94·0	4·7	13·3	26·6	38·7
2	91·5	~0	~0	5·5	2·5
3	88·5	~0	~0	5·9	3·6
4	87·5	0·4	1·9	9·8	7·3
5	85·0	2·6	6·6	18·9	39·2
6	82·5	20·9	21·7	27·8	73·4
7	80·0	107	147	50·5	216
8	78·5	122	163	50·8	258

The values of S are given in *Table 2*. In four cases (samples 2 and 3 at 77° and 90°K) the area was too small to measure. The results for butane are also given graphically as a plot of S against carbon content (*Figure 1*) along with the two sets of results for heats of wetting on coals, for comparison.

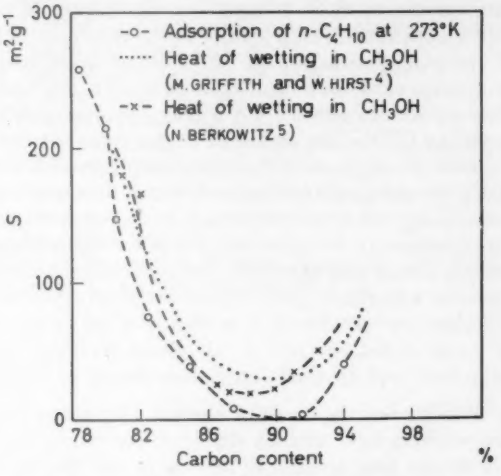

Figure 1. Apparent specific surface versus carbon content

The similarity in general form is striking, particularly in view of the different origins of the samples used.

As will be seen (*Table 2*), the value of S is always significantly greater at 90° than at 77°K and, except at the low-carbon end of the series, is greater again at 195°K; in assessing the values for 195°K it must be borne in mind that they certainly represent an under-estimate and they do not contradict, therefore, the general trend of an increasing S at increasing temperature. The butane values, except in the middle of the range (samples 2, 3 and 4), again fit in with the same trend; the exceptions are probably due to a molecular sieve effect, butane even in its minimum dimension[12] (4·9 Å) being definitely larger than the minimum dimension of nitrogen (3·0 Å).

The results as a whole fit in well with the views of Zwietering[9], and of Maggs[8], bearing in mind the molecular sieve structure of some coals[13] which apparently contain flattish cavities some 40 to 60 Å across, connected with fine capillaries having a cross section very little in excess of the cross section of a nitrogen molecule. Passage through these capillaries would accordingly be an activated process and so would be attended by a high temperature coefficient. It is difficult to assess the energy of activation (E) with any accuracy; but since the adsorbate molecule would be surrounded by the solid walls of adsorbent, E would most probably be larger, perhaps by threefold or more, than the energy of adsorption. A value of E of, say, 7 kcal.mole^{-1}, would thus seem to be reasonable[12]; this would (by the ordinary Arrhenius expression for reaction rate) lead to an increase in rate of 10^3 between the temperatures 77° and 90°K. Thus at the lower temperatures the rate of passage through the fine capillaries would be much slower than at the higher, so that surfaces reached by large numbers of molecules of nitrogen at 90° in the 1 to 3 hour period of a sorption measurement would only be reached by negligible numbers at 77°K.

It is possible, as suggested by Maggs, that the energy of activation E is itself temperature-dependent, being greater at lower temperatures because of the effect of thermal contraction in still further constricting the pores. However, the average expansion coefficient of coals is low[14], of the order of 30×10^{-6}; thus a pore of diameter 4 Å would only contract by 0·0016 Å on cooling from 90° to 77°K. The potential energy between the wall and the adsorbate molecule would have to fall very steeply indeed with distance to alter significantly the energy of interaction between the molecule and the wall. Exact assessment is again impossible in view of our ignorance as to the exact shape of the cross section of the pore and also of the necessary parameters for calculating the attraction and repulsion forces; but for a typical non-polar gas molecule near an adsorbate consisting of a covalent crystalline continuum, J. M. HONIG[15] gives curves whence it is seen that the fall is approximately 0·5 kcal.mole^{-1} over a distance of 3 Å, i.e. about 0·17 kcal.mole^{-1} for 1 Å. Thus the change in E with thermal contraction would be inappreciable.

A remarkable feature of the curve of surface area against carbon content to which other workers have already drawn attention, is the trough in the region of 87 to 92 per cent carbon. In this range the values obtained at the lowest temperatures are small, and indeed with two samples they were too small to measure. Moreover, it is exactly in this range that the values for S at 273°K (i.e. by butane sorption) are less than at 195°K (by nitrogen sorption), contrary to the trend on both sides of this range. The two sets of facts together suggest that in the range in question many of the pores have a diameter smaller than that of the butane molecule, but of the same order of diameter as that of the nitrogen molecule; thus despite the higher temperature the butane molecules still cannot reach the parts of the surface to which the finest capillaries lead.

CONCLUSION

The present work lends general support to the views of Maggs and of Zwietering regarding the interpretation of the values for specific surface of coal as measured by gas sorption. They emphasize that the value obtained is a function both of the adsorbate used and of the temperature of measurement. It is therefore scarcely possible to speak of the 'true' specific surface of the coal or vitrain.

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Recent Developments and Notes

FUEL EFFICIENCY IN INDIA

The Government of India appointed last year a fuel efficiency committee to evolve suitable and adequate measures for achieving optimum economy and efficiency in the use of fuel resources in the country, particularly coal. The committee will work in close coordination with the Department of Iron and Steel as well as with the railways, and will be assisted in matters relating to research and technical investigations by a fuel efficiency cell located in the Central Fuel Research Institute.

Another committee has been set up to make an assessment of the demand for sized hard coke that is likely to arise by 1962 and to estimate the gap between the demand and the availability of hard coke. Consequent upon the rapid industrial expansion in India in the past few years the demand for hard coke has already far exceeded the supply and it will be necessary for the committee to make plans for increasing coal production in order to cover the gap. The committee will also consider whether the required additional quantity of coke can be obtained by expanding the existing coke oven plants including those at Sindri and Durgapur, or whether it will be necessary to establish new units [*Indian Min.* 1958, **12**, 128].

FLEXIBILITY IN THE GAS INDUSTRY

The Secretariat of the Economic Commission for Europe has recently issued a report on *Ways of Improving the Flexibility of the Gas Industry*, prepared by a working party on gas problems [United Nations: Geneva, 1958, 90 pp]. The problem of improving the flexibility of the gas industry is a fundamental one for the industry's development. On the one hand, the flexibility of this form of energy in use is one of its main advantages, but on the other hand, the preservation and improvement of this flexibility set difficult economic and technical problems and the way in which they are solved has very marked repercussions on costs, and hence on the development of the industry.

The problems of seasonal variations are first examined by a statistical analysis, then the methods used to achieve greater flexibility in gas output from both the supply and demand sides. Finally an attempt is made to draw some practical conclusions which may afford useful guidance for the gas industry in the various countries.

A considerable amount of statistical technical and economic information is given for Czechoslovakia, Denmark, Eastern Germany, Western Germany, France, Italy, Poland, Portugal, Spain, the United Kingdom, and the Union of Soviet Socialist Republics. Some of the most interesting and valuable sections of this information are those giving data for the operation of flexible production units complementary to coke ovens and gasworks of the conventional type, for example, complete gasification processes, gasification of petroleum products in special production units, use of petroleum products and natural gas for the production of gas in conventional units.

Meeting variations in the demand for gas is said to be difficult owing to the extent to which the gas industry at present depends on the production of coke oven gas which is not governed by seasonal fluctuations of demand in that industry.

The means envisaged for improving the flexibility of the gas industry are: (*i*) creation of new production units to help to meet peak demands, (*ii*) accumulation of large stocks, (*iii*) encouraging off-peak consumption or restraining peak-period consumption through the medium of tariffs. The study made by the working party is said to prove that the provision of new production units would enable variations in demand to be met, but most of the modern processes have been in operation too short a time to enable accurate predictions to be made as to their economic value in the gas industry. It is suggested that it might be worth while to compare the economic value of the new production units with that of underground storage. The former might be used for covering peaks of short or medium duration, while seasonal variations might be met by underground storage.

D.S.I.R. GRANT FOR SPECIAL FUEL RESEARCH

The *Report* of the Council for Scientific and Industrial Research for 1958 has recently been published [*Report of the Research Council for the Year 1958.* Department of Scientific and Industrial Research; H.M.S.O.: London, 1959]. The main duty of the Council in the past year has been to make proposals for the Department's expenditure under the second five-year plan which runs from 1959 to 1964. The programme for this period which is described in the report entails a total expenditure of £61 million compared with £36 million for 1954 to 1959. There is only one grant, amongst those for special researches which were authorized during the session ended 30 September 1958, for work in fuel technology, and this is to Professor M. W. THRING, of the University of Sheffield, for studies of the formation and combustion of coal smoke, the amount of the grant being £15775 for 5 years from 1 October 1958.

THE STEEL INDUSTRY AND CLEAN AIR

In *The British Iron and Steel Research Association: Annual Report 1958* reference is made to researches which are being conducted on problems arising in the steel industry by the operation of The Clean Air Act. In processes that use oxygen for refining molten blast furnace metal dense brown fumes of iron oxide are emitted. In the Steelmaking Division methods of reducing the amount of fume without greatly reducing the efficiency of the processes are being examined. The injection of steam with the oxygen has been found to reduce greatly fume emission but with undesirable side-effects at times. A possible solution appeared to be offered by the injection of the slag-making materials in the form of a powder with the oxygen and it was thought that the powdered lime, limestone, or iron oxide might absorb some of the heat produced in the reaction zone at the end of the oxygen lance, thus limiting the temperature rise in this zone. Experiments have shown, however, that the amount of iron oxide fume emitted has been appreciably reduced only when the quantities of powdered material added have been far greater than was

necessary for the metallurgical requirements. It is suggested that increasing the area of contact between the oxygen and the molten metal might, by reducing the local rise in temperature, reduce the amount of fume emitted. Experiments are being carried out in which oxygen is blown through multiple jets upon the surface of molten iron flowing along a hot-metal runner to a pig-casting machine. Preliminary experiments have been only partially successful and a fundamental study of fume-formation is now being made by the Chemistry Department.

The Physics Department has continued its work on gas-sampling and gas-cleaning with reference particularly to air pollution by dust and fume. A prototype of the 'LISA' apparatus for the gravimetric measurement of dust and fume content in gases has given reliable results under test. It is now being manufactured by the Longworth Scientific Instrument Company. In gas-cleaning work has particularly been concentrated upon wet scrubbing methods. With a Pease Anthony venturi-type of wet scrubber it has been shown that when water is injected at right angles to the gas stream near the throat of the venturi fume-collection efficiencies of up to 95 per cent can be obtained. If a straight tube is used as an alternative to the venturi tube scrubber section and the water spray is injected concurrently with the gas stream efficiencies of up to 97·5 per cent have been obtained. Further work with this new type of wet scrubber on the pilot plant at the Association's North-East Coast Laboratories is being considered.

NEW ZEALAND'S FIRST OIL REFINERY

Construction is expected to begin at an early date on New Zealand's first oil refinery and a survey is being undertaken to decide upon a suitable site for it. It is to be built by Shell International Petroleum Company Ltd at an estimated cost of approximately £17 million, and the plant will have an annual capacity of 2 million tons.

In preparing its plans, Shell has had to overcome certain unusual problems, in particular New Zealand's peculiar pattern of demand in respect of petroleum fractions, there being a disproportionately high consumption of petrol, and the geographical position of the country, which militates against the economic export of surplus products. The refinery has been designed with sufficient flexibility to process a wide variety of crude oils including, so far as possible, any that may in future be found within the country, if the present search, in which Shell is also participating, meets with success.

CHIEF SCIENTIST TO THE MINISTRY OF POWER

The Minister of Power has appointed Dr C. M. CAWLEY, C.B.E., D.Sc., F.R.I.C., to be Chief Scientist to the Ministry in succession to Sir KELVIN SPENCER, C.B.E., who has retired from the public service.

Dr CAWLEY has been at the headquarters of the Department of Scientific and Industrial Research for the past six years. He has been responsible for administering general policy in relation to the work of the Department's research stations and to grants made by the Department to the Universities and other bodies for the promotion of research and the training of research workers. He joined the scientific Civil Service in 1929, serving on the staff

of the Fuel Research Station until 1953. He will take up his appointment at the Ministry of Power in the early autumn.

PARAMAGNETIC PROPERTIES OF COAL

At the *Fourth Biennial Conference on Carbon*, held 15–19 June 1959, at the University of Buffalo, and co-sponsored by the University and The Carbon Committee, a paper was presented by JEAN UEBERSFELD, of the Université de Besançon, France, on double magnetic resonance in fluids adsorbed on coal. A fluid which contains hydrogen in its molecular constitution, such as water, benzene, toluene, ammonia, or hydrogen sulphide, is adsorbed on coal containing paramagnetic centres. The nuclear magnetic resonance of the protons of the fluid is observed in a static magnetic field. When a microwave magnetic field is applied, the frequency of which is approximately that of the electron spin resonance in the field, an increase in the nuclear resonance signal is observed. This result gives a direct proof of the existence of an interaction between the paramagnetic centres of the coal and the protons of the adsorbed fluid. For coals of low rank this interaction is static and of the 'dipole–dipole' type. For coals of higher rank, the interaction seems to be dynamic and of the 'scalar' type. It is suggested that this experimental technique may be valuable for studies of the surface of coals.

CATALYSIS IN THE GASIFICATION OF CARBON

H. HARKER, of the Northern Coke Research Laboratories, King's College, Newcastle-upon-Tyne, gave an account at the *Fourth Biennial Conference on Carbon* (see note above) of an investigation of the mechanism of the catalysis by alkali-metal salts in the reactions occurring during the gasification of carbon. The immediate objective of the work was to elucidate the nature of the rate-controlling step in these reactions.

The importance of the so-called surface oxide, which is formed simultaneously with gaseous products, is made evident by the results. The formation of surface oxide can markedly reduce electron spin resonance signals in carbons. The oxide appears to be chemically heterogeneous; one component of it, having acidic properties, is stable in the range 300° to 700°C. The application of infra-red spectroscopy and other techniques suggests that the acid oxide consists of carboxyl groups either free or in an anhydride (or lactone) form. The mechanism of catalysis by the salts in carbon–oxygen reactions at 300° to 700°C is not identical with that in carbon–carbon dioxide reactions at 700° to 1000°C; in the former reactions it involves neutralization of the acid oxide and in the latter reactions attack by free metal. The *electronic structure* of carbon is suggested as a general basis for reactivity, surface oxide forming electron 'acceptor' levels which are inhibiting. The catalytic properties of the salts are attributed, in part, to removal of surface oxide, due either to scavenging by free metal or to increased decarboxylation rates. The possibility that the catalysts also function by the formation of independent 'donor' levels is discussed.

WARREN SPRING LABORATORY

The opening of the Warren Spring Laboratory, Stevenage, Hertfordshire,

by the Rt Hon. the Viscount Hailsham, Q.C., Lord President of the Council, took place on 29 June 1959.

In setting up Warren Spring Laboratory 'to carry out process research and development over a wide field not limited to particular areas of technology', the Research Council for the Department of Scientific and Industrial Research expressed their conviction that, when necessary, the Department's Research Stations should change in function and objective to meet the needs of changing situations. The Council considered that the Fuel Research Station at Greenwich had largely fulfilled the aims in view when it was set up, and that current needs were satisfactorily catered for by researches going on elsewhere; they decided, therefore, to close down the Fuel Research Station, and to transfer the staff to a new Laboratory in Stevenage, with new programmes. To ensure that there should be no likelihood of an impression being gained that the Fuel Research Station was being continued at Stevenage, or that the title of the Laboratory might appear to restrict the field of activity, the new Station is named after a lane which used to run across the site. Mr S. H. CLARKE, C.B.E., is the Director of the Laboratory, and Dr C. C. HALL, Deputy Director.

Of the work carried out at the Fuel Research Station only two programmes have been transferred to the new Station, namely, research on the abatement of atmospheric pollution, and on the synthesis of oils and chemicals by the Fischer–Tropsch process. The second of these projects has called for the provision on a generous scale of laboratories, workshops and semi-technical-scale facilities which will give opportunity for much chemical engineering work. But all these facilities can be used for other purposes such as the development on a larger scale of any idea or invention which may arise elsewhere in the D.S.I.R. or indeed in industry itself.

There have been several substantial indications of need for research in the field of mineral processing, and it has been decided that this should form one of the new projects to be undertaken. There have also been indications of need for work on a pilot-scale in various fields which the Department had not been able to meet. With these pointers, it was decided to build a laboratory in a modern industrial style, to be as flexible as possible, to house in the first place a staff about the size of that of the Fuel Research Station, and with facilities for both laboratory research and pilot-scale work [see also *Fuel, Lond.* 1959, **38**, 91].

As regards the programmes of work now to be undertaken in the new Laboratory, the investigations on atmospheric pollution follow naturally from those begun at the Fuel Research Station and are designed to meet the requirements of the Ministry of Housing and Local Government. This work includes further research on the abatement of pollution from boilers, the chemistry of pollutants in the atmosphere, with special reference to possible injurious constituents, the accuracy and reliability of measuring instruments, the distribution and dispersion of pollutants, and cooperative observations of pollution.

The development of oils from coal is a two-stage process, the first involving the complete gasification of the coal to yield a mixture of carbon monoxide and hydrogen, and the second the catalytic conversion of the gas mixture into

the desired end products. The work at Warren Spring Laboratory is concerned only with the second of these stages. The main lines of investigation in this field were outlined in a recent note in this journal [*Fuel, Lond.* 1959, **38,** 230]. The synthesis gas plant to provide the raw material for research at the Laboratory on the Fischer–Tropsch process has been designed and built by Humphreys and Glasgow, Ltd.

The research on mineral processing will include basic investigations on: (*i*) grinding in the presence of additives such as surface active agents, (*ii*) the kinetics of bubble attachments to mineral surfaces, in relation to froth flotation, (*iii*) the behaviour of mineral particles in a high tension field and the effect of various surface treatments.

Chemical engineering problems to be investigated include especially mass-transfer, with a view to obtaining data for the more accurate prediction of the performance of various types of gas–liquid contacting equipment.

UNSATURATION OF OLEFINES

S. S. TIONG and H. I. WATERMAN have recently discussed the determination of unsaturation in olefinic compounds and described a promising method using direct quantitative hydrogenation [*Chim. et Industr.* 1959, **81,** 204 and 357]. The methods depending on the addition of halogens are attended with difficulties due to incomplete addition, substitution, and liberation of added halogen during the determination of excess of reagent. The addition of hydrogen is theoretically the most satisfactory and different catalytic hydrogenation methods, with volumetric or manometric determination of the excess hydrogen, are reviewed. Most of these methods have the serious drawback that uncertain amounts of hydrogen are adsorbed by the catalyst or dissolved in the solvent. Such losses of hydrogen may be appreciable. A considerably improved method was devised by H. A. VAN WESTEN [*Diss. Delft*, 1931; H. I. WATERMAN, J. N. J. PERQUIN and H. A. VAN WESTEN, *J. Soc. chem. Ind., Lond.* 1928, **47,** 363T] but his apparatus was rather complicated and a relatively large amount of substance was required for the determination.

In the new method described, a volumetric one, errors arising from adsorption of hydrogen on the catalyst are eliminated by reducing the amount of catalyst. Using 25 mg of catalyst composed of 10 per cent of palladium on activated carbon, for a consumption of 45 ml of hydrogen, the error due to adsorption is very small. The direct and continuous measurement of the hydrogen used is carried out in a simple apparatus. The reaction takes place in the presence of acetic acid.

The experimental results for a large number of pure substances agree very well with the theoretical values. With some fatty oils there was found to be good agreement between the Wijs iodine value and the iodine value calculated from the hydrogen consumption, if the oils contained only few conjugated double bonds. The presence of non-condensed rings in aromatic compounds does not affect the determination.

PETROLEUM INDUSTRY IN THE U.S.S.R.

T. REIS, Administrateur-Directeur général de *Pétrole-Chimie*, has published an account of his findings on a recent visit to Moscow, of the state of the

Russian petroleum industry [*Chim. et Industr.* 1959, **81,** 619]. In 1945 the production of crude petroleum in the U.S.S.R. was about 20 million tons, 40 million tons in 1950 and 115 million tons in 1958. Between 1945 and 1956 the production of natural gas increased from 3·5 to 30×10^9 m³. In comparison the production of crude petroleum in the U.S.A. in 1957 was about 400 million tons. According to the seven-year plan which was put into operation in January 1959, it is hoped to double the production of crude petroleum, to 230 million tons by 1965, and to increase the output of natural gas by five times, to 150×10^9 m³.

At the present time, according to the data of the author, coal, petroleum and gas are responsible for approximately 59, 24 and 5 per cent respectively of the total energy produced in the U.S.S.R. By 1965 it is predicted that the corresponding percentages will be approximately 50, 27 and 13.

N. KHRUSHCHEV, in his report to the Praesidium of the Central Committee, in the early part of 1958, indicated that he foresaw during the seven-year plan, investments of 4000 milliards of francs in the petrochemical industry, to increase the production of synthetic fibres, fertilizers, plastics, synthetic rubber and other materials. This amount of investments would correspond to increasing the production of chemical works in general by 3 times, of synthetic fibres by 14, plastics by 6, fertilizers by 3 times. New works to the extent of 140 are envisaged, and the modernization of 130 existing works. To produce the increased amount of petroleum and gas by 1965 mentioned above, it is estimated that about 7500 milliards of francs will be invested in the industry.

N.C.B. UNDERGROUND GASIFICATION PROJECT

Since the National Coal Board announced early this year that experimental work at Newman Spinney, near Chesterfield, on the gasification of coal underground, would cease at the end of May, as further expenditure on the project did not appear to be justified, further developments have taken place and the scheme was extended until the end of July [see *Fuel, Lond.* 1959, **38,** 228].

A 3·75 MW power station, built by the Central Electricity Generating Board, has been operating for a few months from gas produced in the underground gasification pilot plant built by Humphreys and Glasgow, Ltd. At the time this plant was planned the 'blind borehole' system of gasification was contemplated [see *Fuel, Lond.* 1958, **37,** 237]. With this system, however, the elaborate underground pipework is rather vulnerable.

Following an interchange of visits between engineers working on this technique in this country and in Russia, a new system has been designed to avoid underground pipework. A shaft was sunk to the coal seam on the site at Newman Spinney and a gallery driven horizontally. From this gallery boreholes were drilled within the coal seam for distances up to 450 ft, a considerable achievement, since the seam is only 27 in. thick and the holes are 14 in. in diameter. Vertical holes were drilled from the surface to intersect the horizontal boreholes at the ends remote from the gallery.

Other boreholes were drilled from the surface to intersect the gallery for primary admission of air to the system. When the system was completed,

ignition was started in the gallery. This was brought about by 'bonfires' of coal and timber ignited electrically from the surface.

The gases resulting from the reaction travel along the boreholes within the seam and back to the surface via the vertical uptakes, and thence by means of surface mains to the power station. The gas is cooled by the direct injection of water, supplemented by surface cooling of the mains.

The new method has shown such encouraging results that the N.C.B. postponed the closing down of the pilot plant to enable more operating experience to be gained. Mr R. LANGFORD, of Humphreys and Glasgow, Ltd, who has been in charge of the project, has recently been to India to discuss with government officials the possibility of introducing in some Indian coalfields some of the methods developed in Britain.

OIL PROSPECTING AND DETECTION IN THE U.S.S.R.

At the Fifth World Petroleum Congress, held in New York, 30 May to 5 June 1959, a paper was presented by YU. N. GODIN, M. K. POLSHKOV, L. A. RYABINKIN, V. V. FEDYNSKY and E. E. FOTIADY on progress in geophysical methods for prospecting for oil and gas in the U.S.S.R. In the last four years the number of geophysical crews exploring for oil has increased almost twofold. Most of the geophysical work was conducted in the Caucasus, the Ukraine, in the eastern regions of the European part of the U.S.S.R., Siberia and Central Asia.

Among the new geophysical instruments produced and used during recent years are the nuclear-resonance magnetometer, the gravity gradiometer, the damped marine gravity meter, apparatus for the study of telluric currents, portable 24-channel seismic stations, apparatus for river and marine seismic prospecting, instruments for controlled directional reception of seismic waves.

At the present time, regional geophysical investigations, used as a guide for further detailed studies, are conducted with a combination of gravity and magnetic mapping and deep seismic soundings of the basic layers of the earth's crust, including the Mohorovicic discontinuity. Such investigations were conducted in Central Asia, the Ukraine, the Russian Platform, the Caspian Sea, the Pacific Ocean, and elsewhere, and in each case they yielded important results. Reflection seismic prospecting remained the principal method of search for petroliferous structures, but it is still very difficult to apply the seismic method in detailed exploration of very gently dipping structures in the Platform region, and other methods are being tried.

In another paper investigations into direct oil detection methods carried out in recent years in the U.S.S.R. were described by V. A. SOKOLOV, S. A. ALEXEYEV, E. A. BARS, A. A. GEODEKYAN, G. A. MOGILEVSKY, U. M. YUROVSKY and B. P. YASENEV. The work comprised the development and application of geochemical, biochemical and radiometric methods of prospecting and exploring oil and gas fields.

The direct geochemical indications of oil and gas considered are natural oil gases, bitumens, bacteria-assimilating migrating hydrocarbons and other

indications due to the effect of migrating gases on the surroundings, as well as organic substances of crude oil origin dissolved in underground waters. Results are given of practical work involving the use of gaseous and microbiological surveying, gas logging, and other methods of exploration. Analysis of the effectiveness of direct oil and gas detecting methods shows that under favourable geological and geochemical conditions the proportion of correct predictions is as high as 70 per cent.

TURBODRILLING FOR OIL

R. A. IOANNESYAN, Research Director, All-Union Scientific Research Institute of Drilling Technique, U.S.S.R., *et al.* described the progress made in turbodrilling and in new drilling methods for oil in the U.S.S.R. in a paper read to the Fifth World Petroleum Congress, held in New York, 30 May to 5 June 1959. The turbodrill is now being used in 86·5 per cent of all drilling for oil and gas. Fast drilling has been achieved by increasing the horsepower and by decreasing the hole size from 11¾ in. to 7½ in. Deep wells can be drilled with turbodrills making 9½ in., 8½ in., 7½ in. and even 5½ in. and 4½ in. holes; these turbodrills are of an improved design, some of them embody turbines made of plastic. New bits have been developed in which the cone bearings are not subjected to the weight on the bit; these solve the problem of efficient bits for small diameter holes. Turbodrills designed for use with diamond bits have likewise resulted in a significant increase in the penetration rate in deep and small diameter holes. Due to improvements in directional drilling techniques, it has become possible to drill three holes simultaneously with one rig.

New deep drilling methods, based on various sources of energy, are in process of development. The use of the electrodrill, in conjunction with air or gas instead of mud as the drilling fluid, results in improved performance under certain severe conditions. Vibro-rotary drilling increases the interval drilled per bit in hard formations. The explosion method can be applied to deep and very hard formations; a continuous and controlled explosion eliminates all mechanical tools in the drilling process. Under study for the same purpose is a method based on hydraulic shock effects, which are produced by electric discharges through a fluid.

NEW PROCESS FOR UPGRADING NAPHTHAS

A new isomerization process for upgrading C_5–C_6 virgin naphthas is being developed by Esso Research and Engineering Co., New Jersey, U.S.A. This was described in a paper by K. P. LANNEAU, W. F. AREY, S. F. PERRY, A. SCHRIESHEIM and H. A. HOLCOMB, presented to the Fifth World Petroleum Congress, held in New York, 30 May to 5 June 1959.

The process employs a highly active catalyst which permits liquid phase operation at low temperature, 27° to 50°C. Equilibrium isomer distribution at this temperature level favours formation of the branched, high octane isomers. The process operates with almost 100 volume per cent yield at high conversion levels, and high octane product is obtained without fractionation or recycle of low octane isomers. Arabian and Louisiana C_5–C_6 feedstock of 84·0 and 89·5 Research (+3 ml TEL per U.S. gallon) octane numbers,

respectively, are converted to isomerized product of *ca.* 98 Research (+3 ml TEL) octane number. The product from the Esso low temperature isomerization process shows excellent blending characteristics in high octane motor gasoline pools. Its high octane ratings and inherent volatility make the isomerized naphtha desirable for blending premium grade gasolines.

FUEL CELL

NRDC Bulletin for April 1959 (National Research Development Corporation; Number 14, p 29) contains a special article by F. T. BACON on the hydrogen–oxygen fuel cell in the development of which the author has made some of the most important advances in the past few years and is now carrying out further work for the Corporation.

To obtain electrical energy directly from a reaction between some kind of 'fuel' and oxygen in an electrochemical cell, without using the steam cycle, has been regarded as an extremely desirable objective for many years past. If such fuel cells could be devised they might well have considerable advantages over heat engines, as power generators. There have been many attempts to use solid or liquid fuels, but the use of such materials presents very serious problems and the results have not been promising. The most recent attempt to develop a cell using carbon as the fuel was made by A. M. POSNER, using a cell of the redox type and working under the direction of Professor Sir ERIC RIDEAL, F.R.S., of King's College, London [*Fuel, Lond.* 1955, **34,** 330]. This work, however, has now been discontinued.

At the present time all serious work in this field is being conducted with gas cells, which show considerable promise. Amongst those prominent in recent times as investigators with this type of cell have been the late Professor BAUR, of Zürich, and O. K. DAVTYAN, of Moscow. Work with a cell consuming pure hydrogen and oxygen, which has the advantage of being a simple system and was known to give encouraging results, was begun in 1938 under the sponsorship of the late C. H. MERZ, and from 1946 to 1956 was continued at the University of Cambridge by the author of the present article, in the latter part of the time in the Department of Chemical Engineering, under the supervision of Professor T. R. C. FOX. The work during this period was financed by The Electrical Research Association and the Ministry of Power. At the end of the period it was considered that the basic research work had proceeded to the point at which the next stage should be the development of a battery which would produce useful amounts of power. The National Research Development Corporation agreed to finance such a project and in May 1957 a development contract was placed with Marshall of Cambridge Electronics Limited.

The project at present has for its objective the construction of a battery which will develop about 10 kW, complete with automatic controls. This will require a battery of 125 cells in series, each cell being approximately 10 in. in diameter. As the largest battery previously constructed has been of 5 in. diameter only, with 6 cells in series, many new technical problems require to be solved. Up to the present time a 10 in. cell has been in operation since March 1958 and useful experience has been obtained with it. A current of 100 A has been obtained at 0·8 V, and 240 A at 0·6 V, at 200°C and 600 lb/in^2.

Up to ten cells in series have been operated so far. Considerable progress has been made but there are still a number of problems to be solved before a completely automatic and reliable battery is produced.

METHANE DRAINAGE FROM COAL MINES

It is announced that the National Coal Board is planning to expand its programme for methane extraction from coal seams. The advances in technique made by the Board in the past few years have been so successful that the present 62 drainage plants in the country are to be increased by about 25 in the next three years. This will double the amount of gas now being drained and quadruple the amount used by area gas boards and in other ways. At present about $1{\cdot}04 \times 10^8$ ft^3 per week are being drained, of which $0{\cdot}42 \times 10^8$ ft^3 are being used, mostly by the gas boards.

It is estimated that about 3×10^8 ft^3 of methane per day are discharged in British mines, representing a heating value of about 10^6 therms per year, equivalent to more than a third of the amount delivered from British gas works [*Daily Telegraph*, 18 May 1959].

ATMOSPHERIC SAMPLING AND ANALYSIS

In a report of Committee D 22 of The American Society for Testing Materials, five new tentative methods are proposed for atmospheric sampling and analysis [Philadelphia; The Society, 1958, *Prepr. 55*, 55 pp]. These tentative methods are: (*i*) test for nitrogen dioxide content of the atmosphere (modified Griess–Ilosvay reaction), (*ii*) test for oxides of nitrogen in gaseous combustion products (phenol disulphonic acid procedure), (*iii*) sampling atmospheres for analysis of gases and vapours, (*iv*) test for inorganic fluoride in the atmosphere, (*v*) test for oxidant (ozone) content of the atmosphere. There is also a revision of the tentative method for the continuous analysis and automatic recording of the sulphur dioxide content of the atmosphere.

NEW NATIONAL COAL BOARD APPOINTMENT

The National Coal Board in April appointed Dr J. BRONOWSKI as Director-General of a new department to take charge of the development of new processes for treating coal and in particular of the development of new processes for making smokeless briquettes from small coal. The Department is called the Process Development Department. Dr BRONOWSKI has until recently been Director of the Board's Coal Research Establishment at Stoke Orchard, where several new processes for briquetting and treating coal have been devised in the laboratory. It is now intended to bring these processes to the state of commercial production as soon as possible.

The new Department is primarily concerned, in the first place, with the development of the following processes:

(*a*) making binderless briquettes by the 'Shape' process;

(*b*) the briquetting of char made from small coal by fluidized carbonization, with a special binder;

(*c*) treating conventional briquettes with mild heat so as to drive off the volatile matter which makes smoke.

The production of coke, 'Phurnacite', conventional briquettes and by-products remains the responsibility of the Board's Carbonization Department, under its Director-General, Dr R. J. MORLEY. This Department also remains responsible for the development of premium smokeless fuels in conventional coke ovens, such as 'Warmco'.

DRAKELOW C POWER STATION

The Central Electricity Generating Board have received the consent of the Minister of Power to the building of the largest power station yet projected in the British Isles. It will be constructed at Drakelow, near Burton-upon-Trent, and will have a total output capacity of approximately 1500 MW.

The Drakelow site is on the fringe of the East Midlands coalfield, which is a major source of the low-grade coals used in the production of electricity. Here a 240 MW station, Drakelow A, was commissioned in 1954 and a second station, Drakelow B, with a capacity of 480 MW is being built. The new station will be known as Drakelow C.

The site of the new station is at a focal point of the 275 kV Supergrid system, and the output of the new station can be fed into the system without the construction of additional overhead transmission lines.

HEATING AND VENTILATING RESEARCH COUNCIL

This organization was only formed in 1956 and has spent most of its first three years laying the foundations of future organization, planning and initiating a research programme, recruiting staff and building up an information service for members.

The Council began its first major research project in the winter of 1956–7. This is an investigation into the problems arising from the intermittent heating of buildings, and it is conducted, with the cooperation of the Ministry of Works, in an office building in central London. One of the main objects is to find out how much fuel can be saved by choosing in advance the appropriate equipment and the programme of the daily heating cycle in relation to the thermal characteristics of the building and the installation. Current experience suggests that the savings may be of the order of 10 to 15 per cent; but experimental data obtained in this study do not substantiate the estimates and it becomes clear that the programme of operation is of great importance in achieving economies. Part of the discrepancy is thought to be due to the thermal capacity of the installation itself—a factor which is not usually taken into account in theoretical estimates. During a 12-hour overnight shutdown of the heating system the building cooled by about one third of the initial temperature difference between inside and outside.

A report has been issued, and information gained so far is understood to have proved of value to members in confirming the extent of the factors affecting control of temperature. Analysis of the data has led to proposals from the research staff for new lines of approach to the problem of control. Work is proceeding on this subject of intermittent heating, and priority is also being given to studies of the operation of automatic controls in heating and ventilation plants, of the design and performance of high-velocity ventilation

systems and of design procedures for high-temperature radiant-heating systems [*Research for Industry 1958*; Department of Scientific and Industrial Research: Her Majesty's Stationery Office, London, 1959].

POROSITY OF COKES AND THEIR REACTIVITY

M. MOUTACH and H. GUÉRIN, of the Laboratoire de Chimie minérale industrielle de la Faculté des Sciences de Nancy et de l'Ecole Nationale Supérieure des Industries Chimiques, have made a further contribution to the study of the reactivity of cokes towards steam at 1000°C [*Bull. Soc. chim. Fr.* 1959, 102; see also *ibid*, 1958, 1008 and *Fuel, Lond.* 1959, **38,** 229]. The objective of the research was to explain the variation of reactivity as a function of degree of gasification. The method described previously has been used to follow the variation of the speed of reaction between steam and different samples of coke during the course of their gasification, and at the same time variations of specific surface and pore structure have been examined. The results are similar to those obtained in experiments on the reactivity of coke towards carbon dioxide. The variation in reactivity of cokes towards steam which occurs according to the amount of gasification that has taken place can be explained by a close, though not proportional, relationship between the reactivity and internal surface. The development of microporosity, which appears as soon as the coke begins to be gasified, is responsible for the observed increase in reactivity. A large number of small pores are postulated as developing rapidly at first, and then gradually disappearing as the proportion of large pores becomes preponderating. Differences in reactivity amongst samples of coke are apparently due to their different propensities for developing microporosity. This difference in formation of microporosity may be ascribed to a certain type of heterogeneity of cokes, depending upon the presence of constituents which are reactive in different degrees.

Experiments carried out under different conditions on the same coke, showed how the reactivity was connected with the development of microporosity and explained why the reactivity of a sample of coke, taken to a predetermined degree of gasification, depended closely on the manner in which the given degree of gasification was obtained.

THE OUTLOOK FOR OIL

E. A. HIGGINS, Supply and Planning Co-ordinator, the Shell International Petroleum Company Ltd, spoke to The Baltic and International Maritime Conference in London, in May, on the outlook for oil in meeting the increasing demand for energy in the next 20 years.

He pointed out that oil is the largest single commodity in international trade. It represents 48 per cent of the tonnage carried by sea last year. In the past two decades there has been a remarkable change of emphasis in the pattern of oil movements across the seas. Before the 1939–45 war the Caribbean was the largest area providing oil for Europe. Venezuela is still the world's largest single exporting country, but the Middle East is now the world's largest exporting area, having overtaken the Caribbean area as a whole. The reserves of the Middle East amount to two thirds of the world's total proven reserves. The proportion of world consumption of oil supplied

by the Middle East is still, however, considerably less than this, about one fifth. The U.S.A., despite its large indigenous production, has become a substantial net importer of oil. With regard to world reserves of petroleum, the ratio of proven reserves to production is constantly increasing.

In meeting the demand for industrial and commercial energy, the proportion contributed by oil in 1920 was very small, but by 1956 it has risen to about one quarter. It is generally agreed that the increase in energy consumption will be at a rate of more than three per cent compound per annum, so that the world will require twice as much energy in 20 years from now as it does today. By 1975 oil and natural gas are expected to be dominating the energy pattern, with a total share of nearly half.

USE OF LIQUID FUEL IN THE GAS TURBINE

For the most part, in industrial and marine applications the gas turbine requires liquid fuel for its operation, and that can be interpreted, at any rate for the present, as some petroleum product. A wide range of petroleum fractions can be considered for this purpose and the final choice depends on convenience, availability and cost. At present it would appear that the vital problem to be solved from a technical standpoint is whether or not a residual grade of petroleum can be used, as such a grade of fuel oil is essential if the gas turbine is to compete economically with other types of prime mover. This is the subject of a paper by R. F. DARLING, of Pametrada (Parsons and Marine Engineering Turbine Research and Development Association), presented to the 'Conference on Major Developments in Liquid Fuel Firing 1948–59', organized by The Institute of Fuel and held in Torquay, 11 to 14 May 1959.

The formidable difficulties in the use of residual fuels arise from the presence of incombustible ash. The amount of ash may vary from zero up to about 0·15 per cent and its composition is subject to wide fluctuation, traces of 30 or so elements having been identified in different fuels. Vanadium and sodium are the major constituents and are mostly responsible, therefore, for the fouling and corrosion of the turbine by the inorganic substances present in such fuels.

The development during the past ten years of methods of preventing turbine fouling and corrosion is reviewed by the author. These include changing from a fine spray to a coarse one, the use of a cyclone combustion chamber, mixing additives with the fuel, and the physical removal of deposits from turbine blading. One or more of these methods may keep both fouling and corrosion within acceptable limits, but there seems no likelihood of a universal panacea being discovered. The liquid-cooled gas turbine is regarded as providing the best hope for the future, as it combines the advantages of present-day gas turbines with a fuel consumption comparable to that a of a diesel engine.

ORGANIC SULPHUR IN FUEL GASES

A study of methods for the identification and determination of organic sulphur compounds in industrial and domestic fuel gases was initiated in 1942 jointly by the Rochester Gas and Electric Corporation and the Institute of Gas Technology, Chicago, and has been continued since 1948 by the Gas

Production Research Committee as part of the PAR (Promotion-Advertising-Research) Plan of the American Gas Association. An account of this work has now been published in a monograph by D. McA. Mason and H. Hakewill, Jr who describe methods which are sufficiently sensitive to permit the determination of sulphur compounds present in concentrations of less than one grain per 100 ft³ of gas ['Identification and Determination of Organic Sulphur in Utility Gases': *Research Bulletin 5*, Institute of Gas Technology, Chicago; January 1959, 51 pp].

Sulphur in the form of organic compounds occurs in these gases and remains to the extent of 10 to 30 grains per 100 ft³ after the usual purification methods have been applied. A reduction of total sulphur to less than two grains per 100 ft³ is desirable as this shows a marked decrease in the rate of deterioration of gas-burning equipment. The problem of removing organic sulphur to such an extent is presented by the recognition that each organic sulphur removal process is effective for the removal of one or more sulphur compounds, but not for all.

The procedures described in this monograph are designed for the determination of: (*a*) mercaptans, (*b*) thiophene, (*c*) carbon disulphide, and (*d*) carbonyl sulphide, as well as any (*e*) hydrogen sulphide that may be present, and (*f*) the total sulphur content of the gas. The analytical scheme consists of treating three separate portions of the gas in three different trains of reagents: train (*i*) combustion in oxygen, absorption of sulphur oxides in sodium bicarbonate solution and gravimetric determination as sulphate; train (*ii*) absorption of (*a*) and (*e*) by cadmium chloride, absorption of (*b*) by concentrated sulphuric acid, removal of acid gas by aqueous sodium hydroxide, combustion in oxygen and gravimetric determination of residual sulphur as sulphate; train (*iii*) absorption of (*a*) and (*e*) by cadmium chloride, absorption of (*b*) by concentrated sulphuric acid, removal of acid gas by aqueous sodium hydroxide, absorption of (*c*) and (*d*) by alcholic potassium hydroxide, combustion in oxygen and gravimetric determination of residual sulphur as sulphate.

Mercaptide sulphur is removed from the cadium chloride precipitate of train (*iii*), and the remaining cadmium sulphide is dissolved and titrated with iodine to determine (*e*) sulphur; (*a*) sulphur is calculated from the latter result and that of the titration of the combined sulphide and mercaptide in the cadmium chloride reagent of train (*ii*). Sulphur present as (*b*) is found from the difference between total sulphur in train (*i*) and residual sulphur in train (*ii*), minus the (*a*) and (*e*) sulphur determined above. Sulphur present as (*c*) and (*d*) is determined from the difference between the residual sulphur in train (*ii*) and residual sulphur in train (*iii*). The differentiation between sulphur as (*c*) and as (*d*) is made by iodometric titration of the alcoholic potassium hydroxide solution in train (*iii*).

The research and experimental evidence on which the selection of procedures has been based is given, and the apparatus and analytical methods are described in detail.

OIL-FIRED BOILER PLANTS

A review of the efficiency with which oil is burnt in Lancashire, Economic

and vertical boilers in a variety of industries was given by D. J. HESLOP, of the National Industrial Fuel Efficiency Service, to the 'Conference on Major Developments in Liquid Fuel Firing 1948–59', organized by The Institute of Fuel and held in Torquay, 11 to 14 May 1959. The tests summarized in his paper, on 180 individual boilers in 96 different plants, were carried out by engineers of N.I.F.E.S. during the period May 1954 to December 1958.

The conclusion drawn from carefully analysed results is that the standard of efficiency leaves much to be desired. Capital expenditure appears in general to be unnecessary but better operation and maintenance could lead to appreciable savings. Pressure-jet burner systems with fixed-jet atomizers were found to be mostly used in plants having more than one boiler. The amount of excess air used is one of the main reasons for inefficiency and mechanized proportioning control is advocated for all plants. At some works there were no instruments, and at many others instruments were not properly maintained and a number were out of service. The results are regarded as demonstrating that the average standard of boiler operation is far lower than it should be, and that there should be better training of boiler operators and better supervision of operatives and maintenance by those responsible for boiler plants.

THE USE OF MODELS IN FIRE RESEARCH

The Committee on Fire Research and the Fire Research Conference of the Division of Engineering and Industrial Research of the National Academy of Sciences–National Research Council is planning a two-day international symposium on the theme 'The Use of Models in Fire Research' to be held at the National Academy of Sciences in Washington, D.C., on 9 and 10 November 1959. The meeting will be concerned with the use of models in predicting fire behaviour on a large scale. Contributions have been announced from Japan, England, France, Germany, and the U.S.A. A more detailed programme and the names of speakers will be available at a later date.

Attendance at the Symposium must necessarily be limited and will be by invitation. Those actively interested in basic research on fire and the spread and growth of fire should indicate their interest and request advance registration cards. Address all communications to Mr D. W. THORNHILL, Executive Secretary, Committee on Fire Research and Fire Research Conference, National Academy of Sciences, 2101 Constitution Avenue, Washington 25, D.C., U.S.A.

HIGHER TECHNOLOGICAL EDUCATION

The London and Home Counties Regional Advisory Council for Technological Education issues annually a *Bulletin of Special Courses in Higher Technology*. This is published in two parts; Part I, giving details of courses held in the autumn term, is issued in July, and Part II, containing information about courses held in the spring and summer terms is printed in December. An annual subscription of 6*s* secures one copy of Parts I and II, and application should be made to The Secretary, Regional Advisory Council, Tavistock House South, Tavistock Square, London, W.C.1.

The purpose of this *Bulletin* is to give publicity to special advanced courses held in the London and home counties region which do not regularly appear in college calendars or prospectuses as part of a grouped course or as subjects offered for endorsement on Higher National Certificates. They are usually part-time evening courses, but full-time courses which are specially arranged and are not of longer than three months duration are also included. There are a considerable number of courses dealing with combustion, flame, and power generation.

W. A. KIRKBY

FIRST YEAR AT THE COKE RESEARCH CENTRE

A joint meeting of the Institution of Gas Engineers, the British Coke Research Association and the Coke Oven Managers' Association will be held at 2.30 p.m. on 11 November at the Institution of Civil Engineers, Great George Street, London, S.W.1, when G. W. LEE, Director of the B.C.R.A., will present a paper entitled 'The First Year at the Coke Research Centre'. Sir FREDERICK SCOPES will be Chairman.

COMBUSTION AND FLAME

Readers of *Fuel* may like to know that the following *Notes* appeared in the September issue of *Combustion and Flame*:

National Fire Protection Conference
Fire retardant paint
B.I.S.R.A. experiments on fuel-oil flames
Measurement of gas temperature and heat flow
High-momentum oil burners

Obituary
Dr Clarence A. Seyler

DR CLARENCE ARTHUR SEYLER died at Ferndown, Dorset, on 24 July 1959, at the age of 92.

Seyler was born at Hackney in 1866, son of a well-known freethinker whose ideas influenced him in later life and eldest of a fairly large family; his sister Athene is still well-known on the London stage. He studied chemistry at University College, London and at the City and Guilds Technical College, Finsbury. After this he became assistant to Dr W. M. TIDY in his water analysis laboratory at the London Hospital, and later assistant to Sir WILLIAM CROOKES. The crucial event which turned Seyler's steps towards his life work in coal was his appointment in 1892 as assistant to Dr WILLIAM MORGAN, Public Analyst in South Wales. On the death of Dr Morgan in 1895 Seyler succeeded him as Public Analyst. He was already an experienced Water Analyst (his first publication on the subject appeared in *The Chemical News* in 1894 and he was elected a Fellow of the Institute of Chemistry the following year). The location of the laboratory at Swansea ensured that the associated private practice was concerned to a considerable extent with coal analysis: this circumstance drew Seyler's attention to the inadequacy of the background for analytical assessment of coal properties and led him to an extensive study of coals. Thus began an association with coal research that was to last for 62 years.

In the same year, 1895, Seyler married Ellen Andrews. There were two daughters.

In 1900 there appeared in the *Proceedings* of the South Wales Institute of Engineers the first version of Seyler's Coal Classification in terms of carbon and hydrogen content, the basic structure of which has persisted through many modifications and improvements, and can still be seen, for example, in the Chart 47B incorporated in the latest edition of *Technical Data on Fuel*. An important point brought out in this Chart is the approximate equivalence (which applies with precision only to the bright coals) of carbon and hydrogen on the one hand, and calorific value and volatile matter on the other, as coordinates for specifying the degree of maturity or rank of a coal. This classification may be said to have developed from the pioneer work of REGNAULT and GRÜNER in the nineteenth century.

In 1922 the Coal Research Club, the original sponsor of this Journal, was formed by Dr LESSING and Professor WHEELER in association with Dr MARIE STOPES and Professor HICKLING. Seyler was invited to join this Club in 1923 and was thus associated with *Fuel* at an early stage in its history. In 1925 he was a British delegate at a Conference on the Constitution and Classification of Coal held at Washington, D.C., and in 1926 became a Founder-Member of the Institute of Fuel. In 1931 Seyler became President and Gold Medallist

(with Bar, 1937) of the South Wales Institute of Engineers. In 1938 he was awarded, by the University of Wales, the degree of Doctor of Science, *honoris causa*, for his contributions to coal research. In 1941 he was Melchett Medallist of the Institute of Fuel and in 1955 was elected first Hon. President of the International Committee for Coal Petrology, a body with which he had been actively associated for many years.

In 1956, the year of his 90th birthday, Seyler was presented with the first Thiessen Medal—struck from a compressed mixture of coke, coal dust and tar—by the International Committee for Coal Petrology for his work in promoting coal research. On this occasion a special meeting of the Coal Research Club was held in his honour and the members presented him with an inscribed silver salver. The presentation was made by Dr MARIE STOPES and many will recall the witty exchanges that accompanied the speeches of presentation and acceptance. The Council of the B.C.U.R.A. presented him with a bound volume of his own poems, but with unwonted shyness Seyler stipulated that this should not be seen by his colleagues. A quotation from them nevertheless appears at the head of Chapter 3 in *Coal Science*, by D. W. VAN KREVELEN and J. SCHUYER, 1957 edition. Finally, Seyler's colleagues in the B.C.U.R.A. presented him with an illuminated scroll containing their signatures.

The researches on coal for which Seyler is best known were carried out from 1924 until 1943 with the aid of D.S.I.R. research grants, and from 1943 to 1957 in the laboratories of the B.C.U.R.A., first at Kingston and then at Leatherhead.

Seyler's scientific work on coal fell into three main divisions: classification, microscopical and petrological examination, and the study of rheological properties in relation to carbonization. No attempt will be made here to discuss his contributions exhaustively; for supplementary accounts reference may be made to the papers of which a full list is appended and to *J. Inst. Fuel*, 1941, **15,** 13; *Coal Research*, No. 6, Dec. 1946, 94; D. H. BANGHAM, *Fuel, Lond.* 1946, **25,** 153; *B.C.U.R.A. Gazette*, 1956, No. 29, 10; and especially E. STACH, *Fuel, Lond.* 1957, **36,** 105.

Coal classification in terms of rank, including the development of comprehensive charts showing the inter-relationship of chemical and technical properties, was of enduring interest to Seyler. One important contribution was the publication of the first triangular diagram showing the connection between maceral composition and elementary analysis—and incidentally between macerals and rock types. Another was the introduction of the concept of 'volatile displacement' (δ_v), which enabled the petrological character of a sample to be assessed—to some extent—from its ultimate and proximate analyses. Seyler also played a leading part in the movement to ensure that chemical and physical researches were carried out not on coal mixtures but on (at least) rock types and preferably on what he regarded as their basic components, the 'macerals'. This led him to a fundamental study of the microscopic appearance of thin sections and polished surfaces in relation to coal composition and to a corresponding concern with systematic nomenclature. Together with Dr M. STOPES, Prof. WHEELER, Dr SINNATT,

Prof. HICKLING and Dr LESSING in this country and their colleagues on the Continent, he was largely responsible for the system now generally accepted in Europe.

Seyler's practical work on coal petrology arose from a fortunate coincidence: in 1923 he examined simultaneously, as part of his analytical duties, a broken iron shackle-pin and a dull piece of anthracite; this gave him the idea of applying metallurgical methods of surface preparation to samples of coal before microscopic examination and he was thus able to extend the method even to the examination of opaque coals of high rank. In that year he published photomicrographs of etched coal superior to any previously available. In 1925 he learned in person from Dr R. THIESSEN the technique of making thin sections of coal, but his main work was always concerned with examination of polished surfaces, the value of which was greatly enhanced when he adopted the procedure of examination under oil immersion introduced by E. STACH and E. HOFFMANN.

The concept of a geometric series of discrete steps in the increase of reflectance of components in a given coal was put forward by Seyler in 1938 after he had further extended his microscopic technique by the addition of a Berek photometer; a further advance attended the addition of an integrating stage, permitting the analysis of coal into percentage amounts by volume of groups with different values of the reflectance. From 1941 onward Seyler engaged wholeheartedly in controversies that even now can scarcely be said to have been finally resolved. The components responsible for the successive reflectance steps in a given piece of coal were identified by Seyler as vitrinite, various species of 'intermediate' and fusinite, the last having the highest reflectance; exinite possessed a very low reflectance outside the geometric series. When with increasing rank a jump in the lowest series reflectance occurred, the corresponding component, in the previous coal the lowest 'intermediate', was in the higher-rank coal identified as the vitrinite; the other components excepting fusinite were also (tentatively) believed to move up a step on the scale of reflectance. Physical separation of the components could not, however, be carried out and direct proof was therefore impossible. Moreover, there was much of the artist in Seyler's make-up, and this system of steps together with his classification chart gave full scope for the production of diagrams possessing an attractive combination of symmetry, simplicity and comprehensiveness. It may be that in some of his later work he was too ready to over-simplify and generalize: it was in this field and also in connection with the reality or otherwise of the discrete steps that differences of opinion were rife. Several later workers claim to have observed these steps, and perhaps as many have not. The facts are in part susceptible to statistical study but even in this opinions have differed. Some claim to have observed a few of the steps but not all. At present the prevailing opinion is in favour of continuous variation of reflectance with rank though with the reservation that discontinuities may exist between the higher ranks of coal.

Later Seyler extended the idea of stepwise changes in the reflectance to carbonized coals. He showed that beyond the vitrinite of the anthracite of highest rank, and fusinite, there was a further component which he named alpha-coke.

All this work provided a great stimulus to the study of coal petrology, and petrological analyses based on it were increasingly used by research workers in the B.C.U.R.A. and elsewhere. With appropriate modifications in interpretation the distribution of reflectance in a sample can be used to deduce these analyses, whether the distribution is expressed as a stepwise histogram or a continuous curve. Another important aspect of this work depends on the sensitivity of reflectance to carbonization temperature. This has been used, for example, to estimate differences in carbonization temperature reached in samples of char or coke. A combination of reflectance values in oil and in air has been increasingly used in recent years by Seyler and others to calculate coefficients of light absorption and refractive index.

The third division of Seyler's researches consisted of his work on the rheological properties of coal. He succeeded in measuring, by a weighted-plunger technique, a flow property analogous to viscosity at temperatures below those at which softening is usually recognized. These measurements were found to follow a logarithmic law of variation with reciprocal absolute temperature, and also made possible a definition of softening point in terms of a precise rheological measurement.

In 1938 and 1939 he was also interested in the ignition of coal and published papers on this subject.

It is much to be regretted that Seyler's constant preoccupation with new work prevented him from embodying his unique knowledge in a book. A good account of his main work may, however, be found in that by W. FRANCIS.

The most noticeable characteristics of Seyler on first acquaintance were his tremendous width of interest, his sense of humour, and his zest for living. He was held in great esteem by his colleagues, assistants and students. Some of his outside activities must be placed on record. He was at one time President of the Swansea Rotary Club, was a Member of the Authors' Club in London and of the Ethical Society, took a practical interest in painting, etching and photography—even taking colour photographs in 1912—and, as already mentioned, wrote poetry. He became an authority on Anglo-Saxon etymology and contributed a number of papers to *Archaeologia Cambrensis*. He applied his scientific and analytical method of approach to the archaeological study of many parts of Great Britain, particularly the Cotswolds, Monmouthshire and his beloved Gower Peninsula in which he knew the name of every field and its derivation. In later life he was, for more than a decade, a Governor of the National Museum of Wales. He took up horse riding in the late 70s and continued until the age of 86.

I was privileged to attend a lecture by Seyler on the first Saturday following my appointment to the B.C.U.R.A. staff. Many memories stand out from the ensuing fourteen years during which we were colleagues: Seyler, in riding habit, striding briskly up the drive of Coombe Springs at Kingston; his 'salty' anecdotes of Bone, Wheeler and other personalities of the early Coal Research Club; his coining of the term 'Bone Age'; his fund of out-of-the-way information on special coal types; his lunch-time demand to newcomers, 'How would you define a rock?'; his original derivation of 'Leatherhead'

from an ancient British word meaning 'grey water'. And perhaps most vividly of all, his account of a meeting with Shakespeare in a train, delivered so convincingly and with such attention to detail that listeners were sometimes in doubt as to whether he believed it himself.

Few have had such a tremendous influence on our knowledge of coal in all its aspects as Dr Seyler. He will be remembered especially for his classification system, an invaluable tool, especially for research workers, for the part he played in bringing order out of chaos in the description of coal types, and for the methods he made available to research workers for selecting samples.

Seyler's unusually full and satisfying life was fittingly ended without ill-health, by a peaceful death while in a coma. He is survived by his wife and two daughters.

I. G. C. DRYDEN

PUBLICATIONS OF DR C. A. SEYLER

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Science in the Use of Coal

A Review of the Proceedings of the Residential Conference held in the University of Sheffield, 15 to 17 April, 1958: published by The Institute of Fuel, 18 Devonshire Street, Portland Place, London, W.1, 50*s* (plus postage 1*s* 9*d*)*

THIS residential conference was noteworthy both for the idea underlying its initiation, that of relating current research to the use of coal, and for the considerable degree of success in the promotion of useful discussion. It has set the seal on what may be regarded as a new look in fuel technology, at least as reflected in the proceedings of the Institute of Fuel. Progress in this branch of technology might very easily have been more rapid if more investigations of a fundamental scientific character had been made, particularly on the gasification of coal and the combustion of fuels. These technological practices are essentially applied physics and chemistry and for too long the technical exponents in these fields have been satisfied with *ad hoc* research instead of attempting to discover the basic scientific principles governing the industrial uses of coal.

The chairman of the committee which organized the conference was Mr R. L. BROWN, the Director of the Basic Research Laboratories of the British Coal Utilisation Research Association. Thirty six papers dealing with hitherto unpublished work were presented to the conference in five sessions. On the physics and chemistry of coal there were nine communications, seven on coal preparation and breakage, ten on carbonization, six on combustion and gasification, four on the reactivity of cokes and chars. In a final session of general discussion an opportunity was provided for an overall assessment of current scientific progress and the present state of knowledge in the above fields.

An analysis of the sources of the communications shows that seventeen were from universities, about twelve of these being reports of investigations sponsored by the N.C.B., C.E.G.B., B.C.U.R.A. and other organizations. Six papers emanated directly from the B.C.U.R.A., five from the N.C.B., three from the Fuel Research Station at Greenwich, one each from the C.T.R.A., B.C.R.A., the Gas Council and two from overseas.

Each session was introduced by one or more surveys of the present position prepared by invited authors. These seven surveys should be of considerable value for some time to come, especially in regard to the suggestions for research which are made in them. Perhaps the most stimulating and suggestive of the surveys presented to the conference is the one on combustion and gasification. Some of the outstanding problems in this field are defined. The kinetics of gas/solid reactions are first considered generally, and then in their application to carbon. The reactions of coal and the modifying effects of the presence of volatiles are next reviewed, and finally the factors to which the

* American price, including postage, $7.25.

reactions are likely to be most sensitive. To determine what is the relative importance of physical processes such as mass transfer and heat transmission, on the one hand, and of particular chemical reactions, on the other hand, as overall rate-determining factors in combustion and gasification processes, constitutes the most important problem in this field.

The Organizing Committee attached considerable importance to their request to authors of papers not only to report the scientific results of their investigations but to discuss also their application or relevance to industrial problems. This request met with a somewhat limited response. In the papers dealing with coal-cleaning processes it is shown how these depend on properties other than density. Bubble attachment, electrical and optical properties, frictional properties, resiliency, friability and particle shape are considered. Mathematics, physics and chemistry can evidently make direct contributions in the study of processes for the preparation of coal. Immediate practical applications appear to arise from the results of an investigation on the factors influencing the bulk density of crushed coal, although in some of the papers in this section the bearing of fundamental investigations reported from Universities upon practical problems of coal preparation was not made evident. It is remarkable that there was no paper presented to the Conference dealing with the industrial approach to coal preparation problems.

Petrological studies of coal in relation to its utilization were reported, especially with reference to carbonization. Petrology and rank must be considered as complementary factors in a sound evaluation and prognosis of the behaviour of a given coal or blend of coals. There are possible fairly immediate practical applications of such studies of coal. Laboratory and pilot-plant researches on the preparation and properties of partially carbonized fuels from high-volatile, weakly caking, bituminous coals, fluid-bed carbonization of low-rank coals, and the carbonization of coal and lignite briquettes, were described, with the preparation of smokeless reactive fuels as their objective.

The papers were in general of a high standard and occupy in the printed report of the conference about 250 pages. The discussions, in which a considerable number of younger scientific workers took part, also visitors from Australia, Belgium, France, Germany, Holland, New Zealand and the United States of America, were undoubtedly stimulating and impressive and the 45 pages of the report devoted to them form an invaluable addition to a publication which must be regarded as an authoritative review of advances in this particular field and indispensable to all concerned with the efficient use of coal. It is perhaps not surprising that references, less than a dozen recent ones, by authors to Russian papers were much fewer than justified by the amount of research on this subject which has been reported in Russian journals in recent years. We may expect this state of affairs to improve considerably now that translations of Russian papers are becoming much more available in western countries.

W. A. KIRKBY

Publications

CHEMICAL ENGINEERING PRACTICE

Volume VI. Fluid Systems II

Edited by H. W. CREMER and T. DAVIES. London: Butterworths Scientific Publications; New York: Academic Press; 1958. *vii* + 600 + *xx pp.* (illus.) 95*s* or $13.30

THE best parts of this volume, as of previous volumes in the series, are those which do in fact deal with practice, as opposed to principles and theories. In many fields of chemical engineering, practice is several fences ahead of theory; it is necessary to make equipment work, whether one understands it or not. Much of the published and accessible work on theory and principles comes from universities, and there is a danger (which will be evident to anyone acquainted with the literature of chemical engineering) of it diverging widely from the important problems of industry. On the other hand, much of the best work done in industry is not published.

To my mind, the most successful section in this volume is 'Evaporation Practice', a strictly down-to-earth account of the subject, likely to be useful to anyone seeking practical advice. Those parts of the sections on gas-absorption which deal with design procedures and the characteristics of industrial equipment would also be useful in practice (much of the material comes from the severely practical little handbook of MORRIS and JACKSON). There are also valuable sections relating to the practical aspects of the liquefaction and fractionation of gases, refrigeration, filters and centrifuges.

The sections devoted to the important subject of fluidization are less useful, perhaps unavoidably. The phenomenon is not well understood theoretically, and the enormous mass of publications on the subject has served to confuse rather than elucidate. The engineering problems involved have been tackled successfully in several industries, but much of the knowledge gained in the process is still subject to commercial security. The definitive account of the principles and practice remains to be written. The survey in this volume will be useful mainly in providing a critical bibliography of published papers on the subject.

It is not possible to review every section of the volume. It was optimistic, to my mind, to expect to deal constructively with 'colloids' in 45 pages. Adsorption, leaching, crystallization, sublimation and freeze-drying are dealt with in a summary fashion. The contents list is as inscrutable as usual.

To sum up, although this volume cannot claim to be definitive or exhaustive with regard to most of the topics touched upon, it will, together with the others in the series, provide an extremely useful first reference for those seeking information about a field strange to them.

P. V. DANCKWERTS

HEAT EXCHANGERS

Applications to Gas Turbines

W. HRYNISZAK. London: Butterworths Scientific Publications; New York: Academic Press, 1958. *xii* + 343 *pp.* (illus.) 63*s* or $10.00

THE commercial success of the open cycle gas turbine operating on constant pressure combustion necessarily depends on the overall thermal efficiency of power production from the fuel consumed. It is well known that to compete with the overall thermal efficiency of the conventional steam cycle with steam turbine which can be of the order of 35 per cent, it is essential for the gas turbine to have an efficient heat exchanger transferring heat from the low pressure combustion products after they leave the turbine to the high pressure combustion air before it enters the combustion chamber and turbine but after the compressor. This requires a very efficient heat exchanger both from the point of view of thermal efficiency and from the point of view of overall size and weight operating with low pressure

waste gases around 300° to 600°C and transferring their heat without any leakage between the two streams to the high pressure air. At first sight this may be regarded as a similar problem to that faced about the middle of the last century by Cowper and others who had to develop an efficient method of preheating the high pressure blast to a blast furnace stove using the blast furnace gas as a source of heat. However, they were able to solve the process by a method involving quite slow reversing systems because the time scale is different and the use of very large stoves sealed in iron cases with hand operated valves for reversing was feasible. These methods are not feasible for the commercial gas turbine.

The interesting thing about this book is that it discusses in full scientific and engineering detail the many solutions which have been considered and to a large extent experimentally tested for the solution of the gas turbine heat exchanger problem at a stage when no one solution can be said to have proved a satisfactory answer to the problem. A very great deal of thought and ingenuity and proper design calculation has gone into many of the methods of dealing with the problem given here and it will obviously be of great value to anyone working on the problem to have such a thorough book. The author is clearly well up in his subject and has studied the literature thoroughly as well as having done many of the calculations himself. He has thus produced a book which is of extreme value for anyone else who wishes to work on this particular problem of designing a heat exchanger of any type known at present for a gas turbine while there is clearly a great deal of information which will be useful to designers of heat exchangers and air heaters for quite different purposes but mainly within the limitation that the hot waste gases providing the heat can be enclosed in metal surfaces. The book is certainly not intended to be a university textbook but even in universities, it is of use for reference purposes because of the thoroughness with which it covers its somewhat limited subject.

There is one rather important point of nomenclature on which the present reviewer would take issue with the author of this book. The reviewer prefers to divide heat exchangers into recuperative, regenerative, and continuous regenerative, the distinction between the first two occurring as to whether the heat passes into one side of the dividing wall and out through the other or back through the same side, while the third type is that in which the heat passes in and out through the same side but the heat-absorbing material is continuously being moved from the heat-absorbing region to the heat-giving-up region, thus the pebble air heater and the Ljungström rotary air heater both come in the reviewer's classification under the heading of 'Continuous regenerators', whereas the author of this book divides all heat exchangers into recuperative and regenerative and then sub-divides regenerative into those with stationary or moving or fluidized matrices respectively. While it is obvious that many methods of classification are possible and indeed all equally good, it would be desirable to reach standardization in this matter.

Besides discussing the many ingenious designs and the methods of calculating the heat transfer and constructional arrangements of these different types of heat exchanger the author completes the usefulness of his work by a series of chapters covering part-load performance, influence of the air heater on the governing of the gas turbine unit, test arrangements, stresses in materials, the importance of initial cost in deciding the most economical size for the heat exchanger, the question of weight for transport gas turbines and other design problems.

To sum up, the book is extremely valuable for those whose work leads them to the design of this particular type of heat exchanger, and of some value to designers of allied types of heat exchanger; but it is definitely a book for specialists.

M. W. THRING

AUTOMATIC MEASUREMENT OF QUALITY IN PROCESS PLANTS

Proceedings of a Conference held at Swansea, September 1957, by the Society of Instrument Technology

London: Butterworths Scientific Publications; New York: Academic Press, 1958. *xi* + 320 *pp.* (illus.) 50*s* or $9.50

IT IS fair to describe as measurement of quality all forms of chemical analysis and measurements of physical properties of streams of liquids, gases and solids, in fact all measurements

except that of the act mass or volume rate of flow. It is also useful to have a conference of papers by specialists in advanced techniques such as measurement of nuclear resonance, x-ray fluorescence and solid thickness (by nucleonic methods) and in new developments of old techniques such as gas calorimetry, pH measurement, oxygen measurement, viscosity or fluid density measurement. Sometimes one wishes there could be a single author who could write a completely coherent book on such a subject, but this is asking too much in this age of specialization. It is likely that such an author would be able to classify his subject matter rather more logically than the material in the papers here, which must have given quite a headache to the conference organizers—as it always does. The headings used describe the subject matter of the papers very well but some papers might equally well have come under other headings; they are: The adaptation of laboratory techniques to plant measurement; Some techniques for gas stream analysis; Liquid stream analysis; Spectrometric methods; Some new techniques for fluid stream analysis; and Measurement of some physical properties. Each paper has a brief discussion which is well worth publishing as in some cases very valuable suggestions are made such as that in Dr MENZIES's paper for using optical absorption in the 1800 to 2200 Å range of wavelengths for measurement of sulphur dioxide and other sulphur compounds.

Your reviewer is sympathetic to the causes of misprints but he was a little disappointed to see a figure labelled 'calorimetric analyser for uranium' which was not in fact concerned with heat measurement but with colour measurement. Perhaps an overall editor might have spotted this one.

In conclusion one can say that this is an extremely valuable book if the user will take the trouble to determine whether the particular measurement in which he is interested is dealt with—there is a subject index and the titles of the papers help, but even so he will be well advised to have thumbed through the whole book beforehand so that he knows when to refer to it.

M. W. THRING

THE SEVENTH SYMPOSIUM (INTERNATIONAL) ON COMBUSTION LONDON AND OXFORD, 1958

Published for the Combustion Institute by Butterworths Scientific Publications: London, 1959. *xlvi* + 959 *pp.* (illus.) £11 4*s*

THE Seventh Symposium has had its discussions, formal and informal. These are certain to have had great influence on plans and on current researches in combustion, for all those who actually took part in the meetings. For these, this volume will serve as a useful permanent source of reference. It records a well balanced spread of subjects, with 31 papers on the Mechanism of combustion reactions, 5 papers on Spectroscopy in flames, 6 on Ionization in flames, 17 on the Structure and propagation of flames, 10 on the Ignition and limits of inflammability, 9 on Interaction of flames and surfaces, 8 on Turbulence in flames, 11 on Combustion in practical flowing systems, 16 on Detonation and its initiation, 5 on Special fuels and 6 on Instrumentation in combustion research. In this very extensive programme, the only obvious gaps refer to heterogeneous combustion, for example, in dust-cloud explosions and in the combustion of powdered solid fuels. The sections on special fuels and on instrumentation in combustion research seem likely to want supplementation fairly soon, to meet the needs of those specially interested in these fields. However, a symposium must be limited to be of maximum use to its participants. In this instance, a considerable degree of success has been achieved in promoting maximum interchange between basic and applied scientists, without inordinate segregation of subjects as wholly 'pure science' or 'applied science'.

For those who did not attend the meeting, but who are concerned with combustion science, the present volume will remain a very valuable source of information, of reference and of suggestive stimuli, for a considerable time. This is particularly true for the sections with many individual papers. In the smaller sections, there are pointers to the exploitation of new fields of research and development, some of which seem likely to grow very considerably in extent before the next Symposium. In particular, sections on ions and electrification in flames, and on marginal detonation, seem likely to attract much further study in their

fundamental as well as their applied aspects. Turbulence in flames, in view of its importance for securing very high rates of combustion per unit volume, seems likewise to grow in importance, more especially in its applied aspects. Again, work on special fuels is only reported in a rather limited way. Undoubtedly there is scope for much more open publication in this field, despite obvious hindrances.

Probably, the problems of solid→gas and gas→solid transformations present one of the least explored fields in combustion research. This is apparent in the matter of pulverized fuels, where the questions have long been under consideration but where really fundamental developments seem to be hanging fire. It is also apparent in problems concerned with the formation of solid products, such as carbon and 'smog' from various hydrocarbon combustion systems, and of solid oxides from various special fuels. All these problems will repay study, and consultation of the records of the Seventh Symposium should prove most helpful. No reference library serving research or development on combustion should be without it. The price is on the high side for a single volume, but the quality of the papers justifies it.

A. R. UBBELOHDE

FUNDAMENTALS OF BOILER HOUSE TECHNIQUE

P. D. DEHNEL. London: Hutchinson, 1959. *ix* + 164 *pp.* (illus.) 25*s*

THIS book deals in the main with the type of boiler found in the industrial field and touches only lightly upon the high duty modern water tube boiler.

Following a brief description of the various types of industrial boiler, the author discusses in some detail such items as boiler auxiliaries and water treatment, and devotes a useful chapter to the formation and properties of steam.

Considerable space is given thereafter to fuels and their combustion, and it is appropriate and indicative of modern times that the author has chosen to include a chapter on the problem of atmospheric pollution.

The author, a lecturer in Fuel and Combustion Engineering, has maintained throughout a good balance between the practical and the theoretical approach. In some chapters a number of worked examples have been given and each chapter ends with a series of questions, with numerical answers where appropriate.

The introduction into the text of the National Coal Board's classification of solid fuel by rank is to be commended in view of its increased use in industry. References to the heat content of solid fuels throughout the book, however, should have been qualified by the statement that the calorific values given are on the dry ash-free basis. A useful addition to the chapter on boiler efficiency and testing, in view of the variability of coal quality these days, would have been to show the effect on efficiency of the variation in ash and moisture content of the fuel.

The brief reference to pulverized fuel practice could, with advantage, have included an illustration of the horizontal type turbulent burner. The reference to the vertical burner tends to suggest that this method of firing is the general rule, whereas in practice its use is confined mainly to the burning of low volatile coals which, in this country, are in a minority.

It is surprising to see in a book of this type so little reference to the use of insulation as a means of reducing losses from radiation. The value of good insulation cannot be too strongly stressed and a short chapter on this subject would not have been inappropriate.

K.E.D.

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted

Verification of the H/C vs M_C/d Diagram

IN A previous publication[1] we presented a revised H/C versus M_C/d diagram. Only the upper part of this diagram was supported by experimental evidence gained from the study of pure model substances, the lower part being obtained by non-linear extrapolation, using the conclusion from H. G. FRANCK's publication[2] that the aromaticity of pitch lies between 0·95 and 1·0.

The line for $f_a = 1$ was thus assumed to be slightly bent, an assumption which aroused comments from B. K. MAZUMDAR *et al.*[3]. Although the basis of Mazumdar's comments was proved to be erroneous[4], it seemed interesting to try and find a model substance having an H/C ratio lower than 1·0 and behaving like an undercooled liquid.

It was found that such an undercooled liquid can be obtained by cooling molten diphenanthryl. On dissolving this in chloroform and adding absolute ethanol, the crystalline form of diphenanthryl (m.pt 187·5°C) is precipitated.

The density of the undercooled liquid diphenanthryl was determined ($d_4^{20} = 1{\cdot}19$) and the value of M_C/d calculated therefrom (10·6). This value was plotted against the H/C ratio (0·64) and fell within the experimental error on the $f_a = 1$ line of Figure 1(a) in our publication[1]. (The value for M_C/d derived from this figure is 10·5, whereas a value of 11·4 for M_C/d would have been found if the line $f_a = 1$ had been straight.)

Further we point out that 1,3,5-tri-α-naphthylbenzene ($C_{36}H_{24}$; m.pt 197·3°C) also forms a glass spontaneously on cooling[5]. J. H. MAGILL and A. R. UBBELOHDE[5] determined the molar volume (393 ml at 20°C) of the undercooled liquid of this substance. From these data the values of M_C/d_4^{20} (10·9) and H/C (0·667) can be calculated. The point corresponding with these values also fell on the $f_a = 1$ line in Figure 1(a).

We consider these experimental facts additional strong arguments in favour of the non-linearity of the $f_a = 1$ line in the M_C/d diagram.

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The Determination of Active Hydrogen in Coal by Deuterium Exchange

A RECENT Letter to the Editor[1] discusses the use of a deuterium exchange method for the determination of active hydrogen in coal. As we have been working on this subject since the beginning of 1956[2], it seems worthwhile to present a short survey of our method together with a review of the results obtained.

The method comprises four main operations.

(*1*) The exchange procedure, which was carried out under varying conditions. The powdered coal (~350 mesh) was brought into contact with:

(*a*) pure deuterium oxide at room temperature for reaction periods of 120 to 290 hours without addition of catalyst, and with addition of acids and bases as catalysts;

(*b*) pure deuterium oxide at the boiling point for the same reaction periods without addition of catalyst;

(*c*) mixtures of deuterium oxide and pyridine in varying proportions at temperatures of from 50° to 140°C for reaction periods of from 50 to 100 hours.

It was found that when no pyridine was used the reproducibility of the results was very poor and, especially for the higher rank coals, rather low (in several cases less than half the acetylation value). With about 70 per cent of pyridine the reproducibility was much better, whereas the results for coals of widely different rank were—with a few exceptions—in good agreement with the acetylation values. The temperature varied from 60° to 80°C. Above 120°C distinctly higher results are obtained, which shows that, in addition to OH groups, other structural units participate in the reaction.

(*2*) The second step was the removal of excess reagent and pyridine. This was done by passing a stream of nitrogen over the sample at 110°C until no moisture could be detected in the exit gas. The amount of reagent solution to be removed from 300 mg coal sample was about 5 ml.

(*3*) Next, the deuterated coal sample was burnt in a normal carbon–hydrogen combustion apparatus and the water formed collected in a tube of special shape at −30°C. Sulphur was retained by silver gauze. The amounts of water formed were about 100 mg.

(*4*) Finally, the deuterium content of the water was determined normally by a method based on the work of H. G. BARBOUR and W. F. HAMILTON[3] and in a few cases by means of the mass spectrometer after reduction. With the former method a drop of about 6 microlitres was used. The rate of fall of this drop through a hydrophobic liquid of slightly lower uniform and accurately constant density was determined and the density of the drop read from calibration curves. A very essential point is the purity of the drop. It was found necessary to expel small amounts of carbon dioxide dissolved in the water of combustion and correct for the 0·1 to 2 microgrammes equivalent of nitric acid (determined by titration on submicro scale) formed during combustion.

A communication on this work was presented at the Round Table Conference on Coal organized by the European Research Associates S.A. (Brussels, November 1958) and at the Gordon Conference on Coal (New Hampton, U.S.A., June 1959).

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Proton Magnetic Resonance of Vitrains at 77·2°K

P. C. NEWMAN *et al.*[1] measured the second moment S_2 of the proton magnetic resonance line for three different coals at 90°K. Their results, which are shown in *Figure 1*, were used by C. L. M. BELL *et al.*[2] in making a tentative estimation of the ratio of (aromatic + methyl) hydrogen atoms to hydrogen atoms in the CH_2 and perimethyl groups. From these values P. H. GIVEN[3], using certain suppositions and corrections, has calculated a ratio of the aromatic to aliphatic hydrogen atoms which differs neither too much from the ratio derived by infra-red analysis nor from that determined on Given's structural model[3] of an 82·1 per cent carbon coal.

As part of a more extensive research programme we measured, by means of a Varian-40 Mc/s wide line spectrometer, at a temperature of 77·2°K, the value of S_2 for a series of vitrains, the compositions of which are given in *Table 1*.

Table 1. Data on the vitrains

Origin	*Ultimate analysis (d.a.f.)%*					*VM (d.a.f.) %*
	C	H	O	N	S	
U.S.A.	71·7	4·9	22·6	0·8	0·4	46·2
France, Lorraine, Faulquemont	80·2	4·9	13·4	1·2	0·6	41·9
Holland, Limburg, Maurits	85·8	5·3	5·3	2·1	1·1	31·0
Holland, Limburg, Emma	88·5	4·9	3·3	2·0	1·2	25·0
Holland, Limburg, Jacoba Sophia	93·7	3·5	1·0	1·4	0·7	8·0
France, Alpes	96·5	1·5	0·7	0·7	0·6	4·0

To exclude the influence of water adsorbed on the coal, the specimens were heated to 165°C under 10^{-5} mm of mercury pressure, until the second moment, measured at room temperature, did not change any more. Newman *et al.*[1] heated their coals to 80°C under 0·2 mm of mercury pressure for 4 hours.

Our results are shown in *Figure 1*. It will be seen that there exists a marked difference in character between our curve and that which can be drawn through the measuring points of Newman *et al.* This difference is not due to the slight difference in measuring temperatures as at 110°K we found a curve of the same character as at 77·2°K.

To examine whether pretreatment of the coal might have any effect, we heated the coal of 80·2 per cent carbon in the same manner as Newman *et al.*, and then found $S_2 = 22{\cdot}8$ gauss[2] at 77·2°K instead of $S_2 = 19{\cdot}0$ gauss[2] as we did after our treatment. So with this particular coal the pretreatment used by Newman *et al.* does not exclude sufficiently the influence of the adsorbed water and for this reason we suppose that their result at 79·2 per cent carbon is too high. The influence of the adsorbed water will be less on their other two coals, because this water is removed the more easily the higher the carbon percentage.

A further interesting point is the value of S_2 at 96·5 per cent carbon. Bell *et al.*[2] took the value of 27·5 gauss² for the contribution to the second moment of hydrogen atoms in CH_2 groups and in CH_3 groups with hindered rotation, and a value of 9·7 gauss² for the contribution of all other hydrogen atoms present in coal. If these values are correct, the minimum value of S_2 should

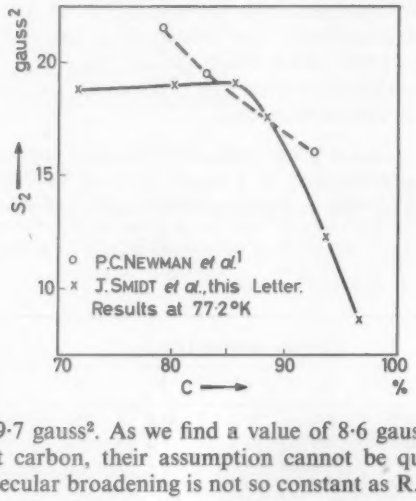

Figure 1. S_2 versus carbon percentage

be 9·7 gauss². As we find a value of 8·6 gauss² for the vitrain with 96·5 per cent carbon, their assumption cannot be quite correct. Perhaps the intermolecular broadening is not so constant as R. E. RICHARDS[4] believes it to be.

For the reasons mentioned above we feel that some scepticism is justified with respect to the conclusions concerning coal structure, which until now have been drawn from the work of Newman *et al.*

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Electronic Absorption and the Energy Gap in Bituminous Vitrain

SOME confusion has arisen recently concerning past attempts to demonstrate the existence and location of electronic absorption in coals. A very good paper was presented recently by R. A. DURIE and R. A. SZEWCZYK on the determination of electronic energy gaps of pyrolysed coals and of a coal vitrain[1]. In their introduction, the authors stated ' . . . the general level of absorption in infra-red spectra of coals . . . appears to increase with carbon content. . . . It is uncertain how much of the absorption is due to structural effects and how much can be attributed to scattering losses due to particle size effects[5]'. Ref. 5 is to R. R. GORDON, W. N. ADAMS, G. J. PITT and G. H. WATSON, *Nature, Lond.* 1954, **174,** 1098. Similarly, I. G. C. DRYDEN[2] quoted the same reference and stated that 'Gordon *et al.* have shown the increasing intensity of background absorption with rank increases due largely to particle scattering rather than to electronic absorption as earlier believed'.

We wish to point out that our data on this subject have been overlooked. Data in Table 3 of our 1956 publication[3] demonstrate electronic absorption by Pittsburgh vitrain beginning near 2 microns. Transmittance decreased from about 70 per cent at 2 microns to 5 per cent at 0·85 micron. This absorption cannot be due to vibration as none of the absorption bands in the 2- to 15-micron spectrum is as intense as absorption at 0·85 micron. No fundamental vibration absorption bands can occur below 2 microns; only weak combination and overtone bands could be present, and these could not cause the observed absorption. As the spectral data were obtained with a

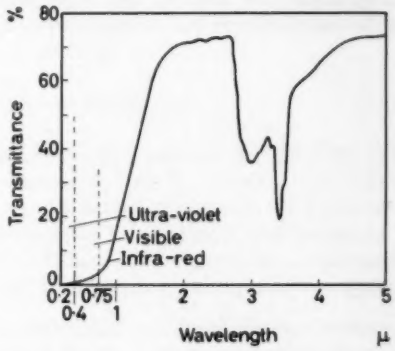

Figure 1. Electronic absorption shown by thin section (0·020 mm) Pittsburgh seam anthraxylon

thin section of vitrain, no difficulties were experienced from scattering by powdered coal particles which interfere badly with potassium bromide pellet spectra or with spectra of oil mulls.

The spectrum of Bruceton vitrain from which the data in ref. 3 were taken is presented in *Figure 1*. Electronic absorption begins at about 2 microns, or or 0·6 eV. The absorption edge or energy gap is difficult to locate because absorption is spread over a rather wide range. The energy gap is at about

0·8 micron, or about 1·5 eV. Dr Durie has kindly informed us that his measurements on a similar coal indicate about the same energy gap.

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The Volatile Residue in Coal Analysis

(*1*) THE fixed carbon (C_f) in high rank coals, calculated from proximate analysis, is often found to exceed the total carbon (C)—generally so for those coals exceeding about 92 per cent carbon—thus implying that for such coals the volatile carbon (C_v) is negative. This discrepancy occurs because, in addition to the usual random errors of analysis, volatile determinations are also subject to a systematic error due to incomplete devolatilization at the volatile analysis temperature (925°C, as specified by *B.S. 1016: 1957*, Pt II). As the quantity of volatile material remaining, which may be termed the volatile residue V_r, is of the order of 2 per cent, this will obviously make a considerable difference to the values of C_v in the whole of the anthracite range, though the importance of the error decreases with decrease in rank. Of course, whether or not the volatile and volatile carbon percentages have such real significance that they deserve accurate measurement is arguable; but on the other hand, if these two parameters are not measured accurately in the first instance, it is difficult to see how their real significance (if any) can be accurately assessed. For example, the volatile carbon is thought[1] to be a major factor in smoke formation, but the use of C_v in any quantitative assessment is hampered by errors derived from errors in V, and hence in C_f. There seems to be a case therefore for determining the volatile residue, V_r, as a correction factor to the nominal or apparent volatile percentage.

(*2*) The volatile residue is best obtained by a carbon (all assumed involatile) analysis of the volatile button and, in *Table 1*, col. 11 shows the values on a dry ash-free basis (d.a.f.) obtained in this way on a set of 10 coals. The values listed are the residue percentages of volatile matter found in the *volatile button* (v_r) comprising roughly 1 per cent of both hydrogen and nitrogen, so that the residue as a percentage of the original coal on a dry mineral-matter-free basis (d.m.f.) is given by

$$V_r = v_r\,(1 - V/100) \qquad \ldots\ [1]$$

where V is the nominal or apparent volatile percentage; the total volatile percentage is then given by the sum of V and V_r (*Table 1*, col. 12). The d.m.f. analysis was calculated from the equation given by F. FEREDAY and D. FLINT[2]. As there is reason to believe (see below) that v_r is a constant for all coals, having an average value (from *Table 1*) of 2·6, equation 1 can therefore be used as a correction factor for all coals, with v_r taking this average value.

(*3*) The above postulate of the constancy of v_r is based on two independent but similar observations. The first is D. W. VAN KREVELEN'S[3] observation that, when coals are progressively carbonized, their analyses plotted on a suitable chart first form individual carbonization tracks that converge on a common carbonization pole (at about 95 per cent carbon, corresponding to a material of composition $C_{100}H_{25}O_2$); but that after passing through the pole the carbonization track is common. This implies that all coals carbonized at a common temperature high enough to take them through the pole will have a substantially similar composition, i.e. v_r will be the same for all coals. The same conclusion may be drawn from the semi-log carbonization plots given

Table 1. Coal analyses

Source	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
	— 'As received' —				Pure coal (d.m.f*) basis											
	Volatile	*Moisture*	*Ash*	CO_2	C	H	O	N	S	$V_{app.}$	V_r	$V_{tot.}$	C_f	C_v	C_v/C_f	*B.S Swelling No.*
(1) *Stanllyd (Blaenhirwaun)*	7·9	1·3	2·9	0·73	93·00	3·35	1·59	1·33	0·73	7·6	2·5	9·9	90·1	2·9	0·03	*N.C.*
(2) *Five Foot (Deep Duffryn)*	12·6	0·9	3·9	0·26	91·80	4·08	2·32	1·42	0·38	12·9	2·3	14·9	85·1	6·7	0·08	1
(3) *Two Foot Nine (Not known)*	28·9	0·8	22·2	13·3	91·20	4·35	2·54	1·65	0·26	26·9	(2·6)	(28·8)	(71·2)	(20·0)	(0·28)	1
(4) *Red Vein (Ciely)*	20·5	1·0	1·6	0·04	89·70	4·66	3·55	1·67	0·42	21·0	2·9	23·3	76·7	13·0	0·17	6½
(5) *Garw (Cwm Tillery)*	27·7	1·0	3·7	0·05	88·90	4·99	4·50	1·33	0·28	28·9	2·4	30·6	69·4	19·5	0·28	4
(6) *Silkstone (Elsecar)*	39·6	1·3	1·7	0·35	86·90	5·79	5·50	1·51	0·30	40·1	2·4	41·5	58·5	18·4	0·49	4½
(7) *Winter (Grimethorpe)*	36·0	2·6	1·7	0·77	84·00	5·47	8·29	1·85	0·39	37·3	3·2	39·3	60·7	23·3	0·38	3
(8) *Cowpen (Northumberland)*	34·6	7·3	4·1	0·95	82·70	5·40	9·60	1·80	0·50	38·5	2·7	40·2	59·8	22·9	0·38	1
(9) *High Hazel (Thorne)*	36·7	5·1	1·0	0	81·90	5·57	10·52	1·58	0·43	39·1	2·6	40·7	59·3	22·6	0·38	1
(10) *Lorraine (Faulquemont*	35·0	5·0	5·9	0·52	79·25	5·13	14·16	0·95	0·51	38·9	2·2	40·2	59·8	19·5	0·32	*N.C.*

* See ref. 2.

elsewhere[4] which show the variation of the two ratios: H/C_f and C_v/C_f for four different coals as a function of temperature (data: R. E. FRANKLIN[5]). These plots seemed to indicate that when individual coals reached their decomposition temperature, the points, if plotted as stated, lay upon a common line so that carbonization at some common high temperature should reduce all coals to a substantially similar composition.

(*4*) The ratio C_v/C_f has also been proposed[6] as a rank index. As *Table 1* shows (cols 15 and 6) this ratio seems to follow the hydrogen and, when plotted against carbon percentage, shows something of the same peak (at 85 per cent carbon); but in contrast to the behaviour of the hydrogen it reaches zero at about 93 per cent carbon as required by the Two-Component hypothesis of coal constitution whereas the hydrogen only reaches zero at 100 per cent carbon.

I am most grateful to Messrs A. Parr-Burman and R. V. Gillespie, of United Analysts Ltd, for their very careful analyses of the coals and more particularly of the volatile buttons; and for permission to publish this note, from the Electricity Supply Research Council and Professor M. W. Thring.

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